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SYNTHESIS AND STRUCTURE-ACTIVITY CORRELATION OF ADDITIVES FOR PERFLUOROPOLYALKYLETHER BASE FLUIDS

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Seventeen novel phosphates/phosphonates were developed as potential additives for perfluoropolyalkylether fluids to inhibit thermal oxidative degradation (in the presence of metals), to provide rust protection, and to enhance lubricity. The materials comprised aromatic phosphates and phosphonates as well as partially esterified compounds, wherein the benzene rings were substituted by perfluoroalkyl and perfluoroalkylether chains. The effects of the substituents on materials' hydrolytic stability and solubility in perfluoropolyalkylether fluids, Krytox 143AC, Demnum S-100 and Fomblin Z25, were determined. The optimum composition, identified to provide thermal oxidative degradation inhibition (at 330°C, over 24 h in the presence of metals), rust protection and lubricity enhancement was a mixture of: $\{C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O\}_2P(O)OC_6H_5$ and $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OP(O)(OC_6H_5)OH$.

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FOREWORD

This report was prepared by Technolube Products Division, Lubricating Specialties Co., Vernon, California, under Contract No. F33615-90-5917 "Synthesis and Structure-Activity Correlations of Additives for Perfluoropolyalkylether Base Fluids" and covers work performed during the period 27 July 1990 through 13 December 1996. The investigations were carried out by K.J.L. Paciorek, Project Manager, with contributions by R.H. Kratzer, S.R. Masuda, W-H. Lin and J.H. Nakahara of Technolube, and J.G. Shih of Ultrasystems Defense. This contract was administered under the direction of the Wright Laboratory, Materials Directorate with Dr. William M. Warner (WL/MLBT) as Project Engineer.

1. EXECUTIVE SUMMARY

The goal of the subject contract was to develop novel additives for perfluoropolyalkylether fluids to inhibit thermal oxidative degradation and corrosion in the presence of metals, to provide rust inhibition and enhence lubricity. The additives were to possess good solubility in the base fluids, down to -40°C, and to exhibit low volatility at elevated temperatures up to 330°C. Ideally, all the properties were to reside in a single composition to avoid compatibility problems.

The investigations were centered on phosphates, phosphonates and corresponding di- and monoesters. Seventeen new compounds and three active mixtures, containing partially esterified phosphates and phosphonates were synthesized. Their effectiveness in inhibiting thermal oxidative degradation/corrosion and rust formation, as well as low temperature solubility, were determined in three commercial fluids: Demnum S-100, Krytox 143AC and Fomblin Z25. The alloys studied were M-50, Pyrowear 675 and Ti(6Al,4V). The effects of perfluoroalkyl and perfluoroalkylether substituents and their chain lengths on the above mentioned properties were also studied. Based on these investigations Additive XVI-AS, which is a mixture of 70-95% of $\{C_3F_7[OCF(CF_3)CF_2]_3O\}_2P(O)OC_6H_5$ and 5-30% of $C_3F_7O[CF(CF_3)CF_2]C_6H_4OP(O)(OC_6H_5)OH$, was found to represent the optimum system. It combined all the delineated characteristics and arrested totally the degradation of Demnum

S-100 fluid in the presence of ferrous and titanium alloys at 330°C over 24 h in oxygen atmosphere. Systems derived from Additives VII, $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)OC_6H_5$, and VIII, $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)C_6H_5$ offered additional potential candidates. The main advantage of VIII lies in its lubricity enhancing characteristics, based on work done by the Air Force. The materials developed under subject contract comprise the best additive system known to date for perfluoropolyalkylether fluids. The program was thus fully successful in achieving and actually exceeded its goals.

2. INTRODUCTION

The objective of this program was to develop novel additives for perfluoropolyalkylether fluids which, ideally, would combine rust, corrosion and thermal oxidative degradation inhibition together with lubricity enhancement. Perfluoropolyalkylethers as represented by the three major families of fluids, namely Krytox, $C_3F_7[OCF(CF_3)CF_2]_xC_2F_5$ [Ref. 1], Demnum, $F(CF_2CF_2CF_2O)_xC_2F_5$ [Ref. 2], and Fomblin Z, $CF_3(OCF_2CF_2)_x(OCF_2)_yF$ [Ref. 3], because of their wide liquid ranges, high viscosity index and thermal oxidative stability, are candidate lubricating fluids for applications where extremes of temperature and environments are encountered. However, due to the fluorine/metal affinity, the presence of metals at elevated temperatures (in particular, in oxidizing atmosphere) or under boundary lubrication promotes perfluoroalkylether degradation [Ref. 4, 5]. The action was found to be arrested by phosphines, phospha-s-triazines, and diphosphatetraazacyclooctatraenes [Ref. 4]. None of these materials exhibited rust inhibition. The only rust inhibitor known at this time was a proprietary product of Montedison. Using chemically different additives for the different inhibition functions presents compatibility problems. Other aspects which needed to be addressed were additive solubility and volatility.

Since phosphates are known to possess lubricity enhancing characteristics, and as phosphines and phospha-s-triazines do

exhibit thermal oxidative degradation inhibiting action for perfluoropolyalkylethers, it appeared conceivable that this property might persist in perfluoroalkyl substituted phosphates and/or phosphonates, inasmuch as the latter does embody the P-aromatic linkage. Furthermore, the presence of oxygen does provide polarity believed to be necessary for rust inhibition. Based on these considerations, the investigations were centered on the syntheses and evaluations of phosphates and phosphonates. Different types of phosphonates were investigated with respect to ease of synthesis. A great deal of effort was devoted to finding an acceptable route to the most important intermediates, namely the perfluoroalkylether-substituted phenols.

The program was successful in developing degradation, corrosion and rust inhibitors superior to most materials currently known. In addition, based on the Air Force studies these materials exhibit also lubricity enhancing characteristics. Thus the objectives of the program were fully met.

3. RESULTS AND DISCUSSION

The synthesis aspects of this program were centered on the development of routes to phosphates and phosphonates and partially esterified materials soluble in perfluoropolyalkylether fluids. The candidate materials were then evaluated with respect to their hydrolytic stability, thermal oxidative degradation inhibition, rust preventing properties and shelf life stability in a fluid formulation. Accordingly, for ease in presentation, the technical discussion was divided into sections addressing these topics.

3.1 SYNTHESIS

Based on past investigations of additives for perfluorinated fluids, incorporation of appropriate perfluoroalkyl or perfluoroalkylether chains was mandatory to render the candidate phosphates/phosphonates soluble in the fluids. On the other hand, direct attachment of fluorinated moiety to phosphorus results in low thermal stability due to preferential PF bond formation. To avoid this problem, $P\text{-}C_6H_4R_f$ and $P\text{-}OC_6H_4R_f$ were the only linkages considered. The potential candidates were thus limited to $(R_fC_6H_4)_{3-x}P(O)(OC_6H_5)_x$, $(R_fC_6H_4O)_{3-x}P(O)(C_6H_5)_x$ and $(R_fC_6H_4O)_{3-x}P(O)(OC_6H_5)_x$.

3.1.1 Initial Investigations

The most direct route to phosphonates is the reaction of an organometalic, such as $R_fC_6H_4MgBr$ with an appropriate chlorophosphorus compound such as $ClP(O)(OC_6H_5)_2$ i.e.:

$$R_fC_6H_4MgBr + ClP(O)(OC_6H_5)_2 \longrightarrow R_fC_6H_4P(O)(OC_6H_5)_2$$

The precursor $p\text{-}C_2F_5C_6H_4Br$ was ready prepared in a 60% yield using the procedure described by Tamborski [Ref. 6] as shown below

$$p\text{-}CF_3CO_2C_2H_5 + LiC_6H_4Br \longrightarrow p\text{-}CF_3C(O)C_6H_4Br$$

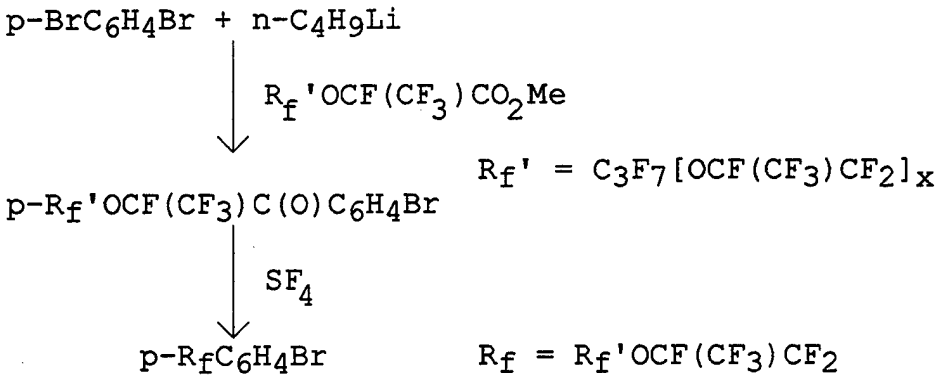
$$p\text{-}CF_3C(O)C_6H_4Br \xrightarrow{SF_4} p\text{-}CF_3CF_2C_6H_4Br$$

Unfortunately, the next step gave a mixture of products:

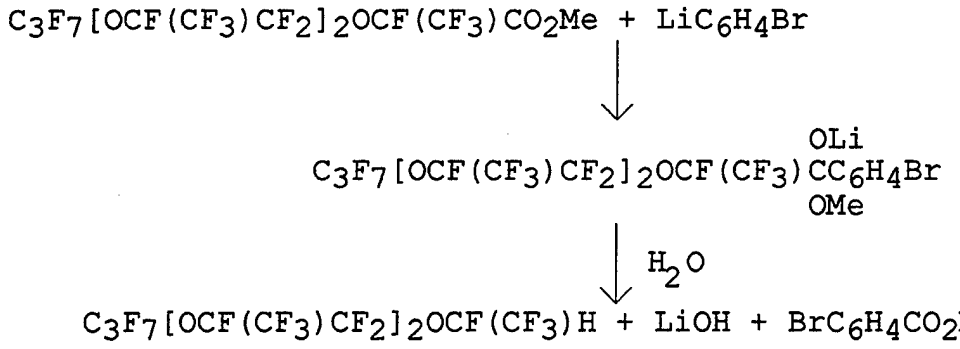
$$C_2F_5C_6H_4MgBr + ClP(O)(OC_6H_5)_2 \xrightarrow[(0°C)]{-7°C} \begin{array}{lll} (C_2F_5C_6H_4)_3P(O) & 5\% & (2\%) \\ (C_2F_5C_6H_4)_2P(O)(OC_6H_5) & 12\% & (19\%) \\ (C_2F_5C_6H_4)P(O)(OC_6H_5)_2 & 55\% & (49\%) \\ (C_6H_5O)_3P(O) & 16\% & (26\%) \end{array}$$

The desired compound, $(C_2F_5C_6H_4)_2P(O)OC_6H_5$, comprised only 55% of the mixture obtained by conducting the reaction at -7°C. The result shows that disproportionation occurs to a very significant degree. Attempts to utilize bromophenyls substituted by perfluoroalkylether chains, such as $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4Br$ were completely unsuccessful due to difficulties in preparing the Grignard, $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4MgBr$. The major product of the reaction was the coupled compound $[C_3F_7(OCF(CF_3)CF_2)_2C_6H_4]_2$.

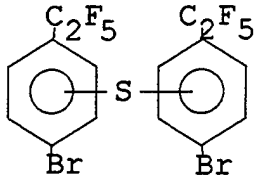
Following the basic process depicted below the intermediate p-$C_3F_7[OCF(CF_3)CF_2]_2C_6H_4Br$ was obtained in a 71% yield:



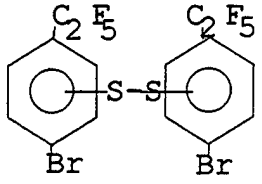
Some problems were encountered in the syntheses of p-$R_fC(O)C_6H_4Br$ intermediates due to the formation of byproducts which lowered the yields and caused difficulties in product separation. In the preparation of p-$C_3F_7[OCF(CF_3)CF_2]_2OCF(CF_3)C(O)C_6H_4Br$ two of the undesired solids were isolated and characterized as p-$BrC_6H_4CO_2H$ and p-$BrC_6H_4CO_2CH_3$. The volatile liquid byproducts were composed of $C_3F_7[OCF(CF_3)CF_2]_2OCF(CF_3)H$, $C_3F_7[OCF(CF_3)CF_2]_2OCF(CF_3)CHO$ and small quantities of other unidentified materials. Formation of the hydrogen-terminated compound, $C_3F_7[OCF(CF_3)CF_2]_2OCF(CF_3)H$, p-bromobenzoic acid and its ester indicate that the expected intermediate was possibly decomposed during hydrolysis by a route different than that leading to the desired product, p-$C_3F_7[OCF(CF_3)CF_2]_2OCF(CF_3)C(O)C_6H_4Br$.



To achieve high yields in the fluorination step, it was found necessary to conduct the SF_4 reaction at moderate temperatures, 100-110°C. Originally, the process was carried out at ~200°C. This resulted in the formation of aromatic sulfur compounds shown below, which were identified among the products formed in the fluorination of $CF_3COC_6H_4Br$.



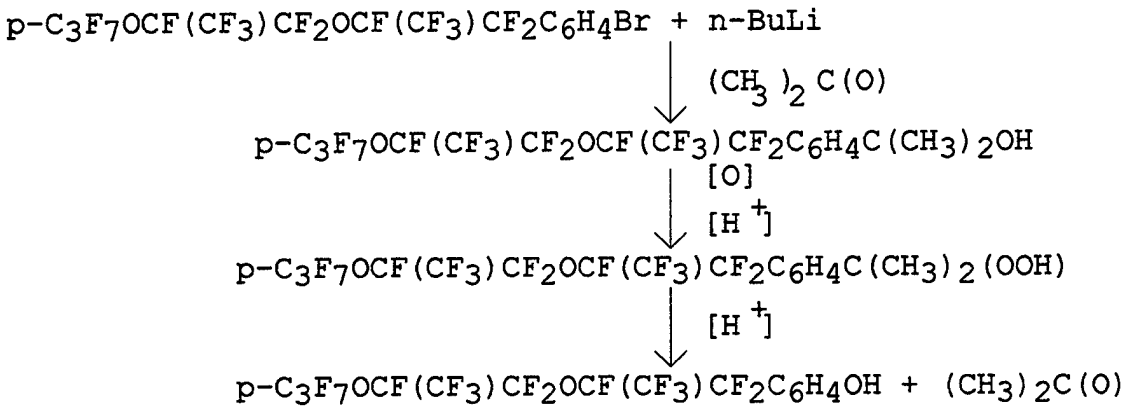
and



Due to the failure to easily obtain p-$R_fC_6H_4P(O)(OC_6H_5)_2$ materials, subsequent efforts were devoted to the syntheses of phenols, $R_fC_6H_4OH$, which were expected to lead to phosphates and phosphonates of the general structure $(R_fC_6H_4O)_{3-x}P(O)(OC_6H_5)_x$ and $(R_fC_6H_4O)_{2-x}P(O)(C_6H_5)_x$, respectively. A number of different potential procedures were investigated to obtain phenols from p-perfluoroalkyletherbromobenzenes.

An important phenol synthesis utilizes cumene (isopropylbenzene), which is first converted into cumene

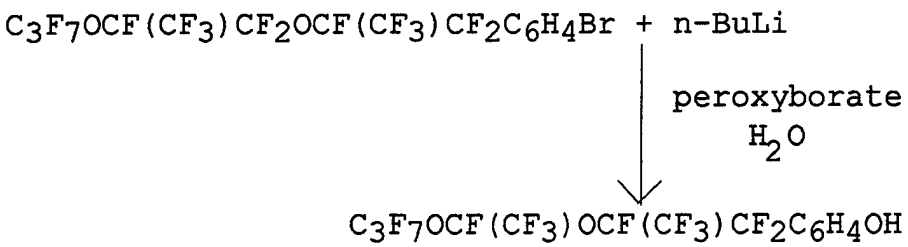
hydroperoxide, and then by the action of aqueous acid into phenol and acetone, i.e.:



The first step, proceeded successfully as shown by the isolation and identification of the acetone reaction product, the tert-alcohol. The conversion of the tert-alcohol into hydroperoxide followed by the rearrangement to phenol was conducted as a one pot process without isolation of the hydroperoxide intermediate. The reaction was only partially successful; some of the desired phenol was formed, but the major product was $p\text{-}C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4C(O)CH_3$, which is derived from the methyl instead of phenyl migration. The relative ratio of the phenol to the ketone was ~1:2. Two possible factors can be responsible for this finding: (1) an electron-withdrawing group at the para position is known to retard migration; (2) the bulky perfluoroalkylether group could hinder the phenyl group migration. As the net result the methyl is apparently the more readily migrating group, forming preferentially

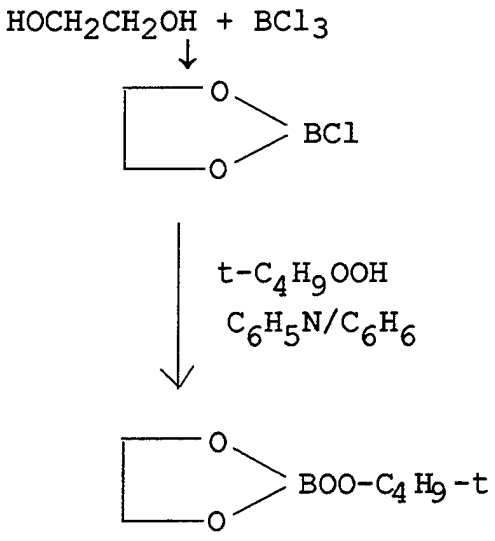
$C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4C(O)CH_3$ instead of the desired $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4OH$.

Another potential process utilizes the oxidation of p-perfluoroalkyletherlithiobenzene [Ref. 7]:



The p-perfluoroalkyletherbromobenzene was first treated with n-butyllithium to generate the lithio intermediate, which was then added to the peroxyborate reagent.

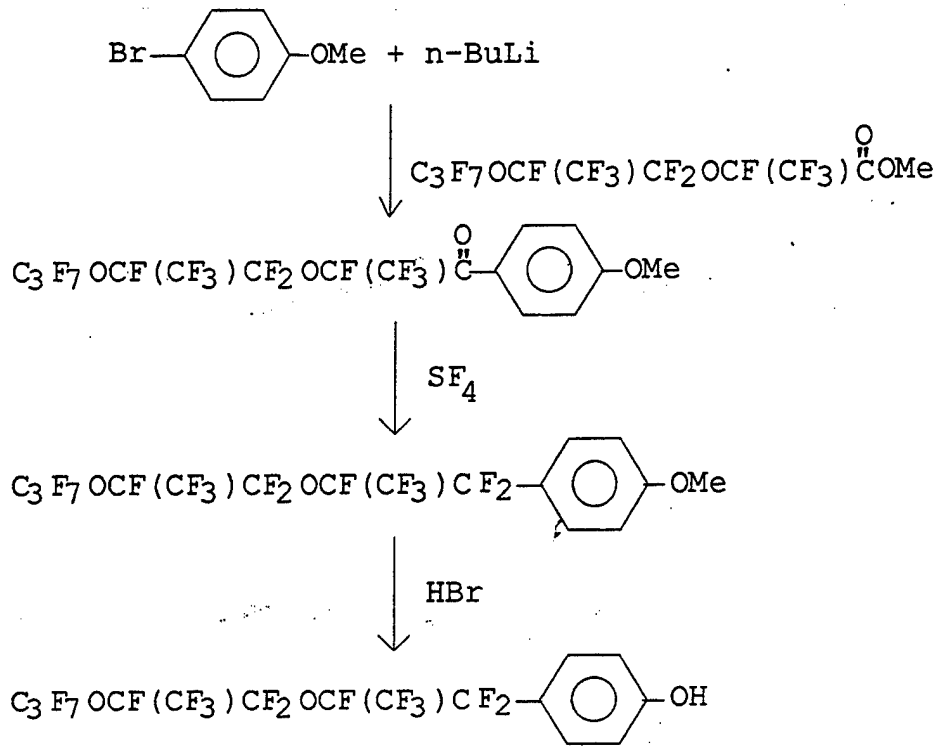
Since the peroxyborate reagent is not commercially available, it was prepared according to a reported procedure [Ref. 7, 8]:



Anhydrous ethylene glycol was first reacted with boron trichloride to afford ethylene chloroboronate, which was then treated with t-butylhydroperoxide in benzene in the presence of pyridine.

Two separate experiments were carried out using this reagent. In both instances only a small quantity of the phenol was detected; the major product was $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_5$. There are a number of explanations for this finding: (a) hydrolysis of the lithio-compound, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4Li$, by moisture present in the peroxyborate reagent (the latter was not amenable to purification.); (b) lack of reaction of the lithio compound with peroxyborate due to the electron withdrawing effect of the `perfluoroalkylether group, giving on isolation the perfluoroalkyletherbenzene; and (c) limited rearrangement of the phenyl-peroxyborate intermediate, specifically the migration of the perfluoroalkyletherphenyl group from the initial location on boron to oxygen. With respect to (c) a similar problem was encountered in the cumene hydroperoxide rearrangement discussed earlier. In view of these difficulties this route was also abandoned.

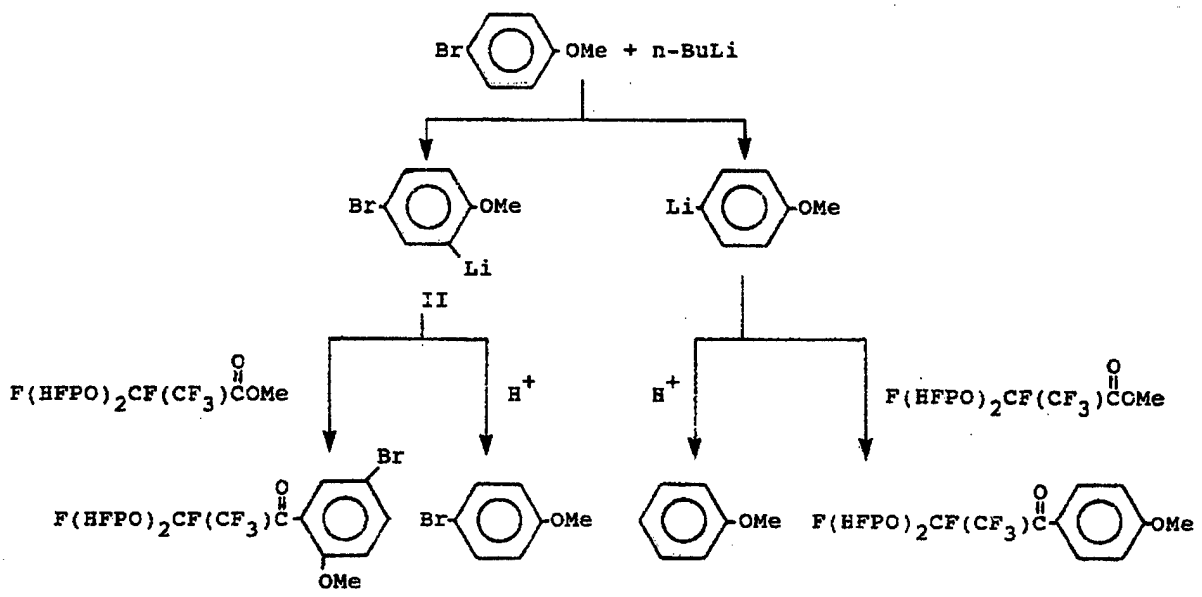
An approach having a hydroxy group prepositioned on the aromatic ring, but protected, appeared to offer another avenue, i.e.:



Accordingly, the p-bromoanisole was treated with n-butyllithium to generate the p-lithioanisole intermediate. The reaction failed to occur at -78°C. Only when the temperature was raised above -45°C the transmetalation started to take place. At ~0°C an acceptable rate of conversion was observed. However, even with prolonged stirring at ~0°C and a large excess of n-butyllithium, the transmetalation failed to go to completion as evident by the persistent presence of p-bromoanisole.

Treatment of p-lithioanisole with the perfluoroalkylether methyl ester gave as the major product the desired $p\text{-}C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)C_6H_4OCH_3$; however, a substantial amount (~20%) of a by-product, perfluoroalkylether-2-methoxy-5-bromophenylketone, was also observed. Its formation explains the persistent presence of the starting p-bromoanisole in the

transmetalation reaction. The p-bromoanisole, due to the presence of methoxy group, is ortho/para directing in electrophilic substitution reactions. The ortho proton is sufficiently acidic to be abstracted by the base ($C_4H_9^-$) to form the 2-lithio-4-bromoanisole intermediate as depicted in the following scheme:

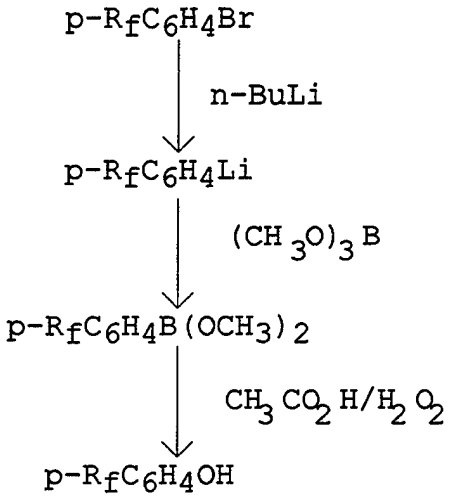


Upon quenching with acid, this intermediate will regenerate the starting material. Hence, neither prolonged stirring nor an excess of n-butyllithium can affect on the transmetalation reaction after 3-lithio-4-methoxybromobenzene has been formed. The next step was the fluorination of the reaction mixture using sulfur tetrafluoride. This reaction failed to give even a trace of the desired product. Thus this synthesis path was also abandoned.

3.1.2 Adopted Phenols' Synthesis

The procedure leading to perfluoroalkylether-substituted phenols, which was finally selected was originally described by Kidwell et al [Ref. 9] and is depicted below:

R_f = C_2F_5 or
$C_3F_7[OCF(CF_3)CF_2]_x$
x = 2,3, and 4



Initially the yields of the desired phenols were very low; however, by modifying reaction conditions, yields above 70% of the pure product were achieved. Based on the properties of the derived phosphates, phosphonates and related materials, the major effort was concentrated on the optimization and scaleup of the synthesis of p-$C_3F_7[OCF(CF_3)CF_2]_xC_6H_4OH$ wherein x = 2 and 3. Reproducible yields of >75% were realized.

In the case of n-$C_8F_{17}C_6H_4OH$, the phenol was obtained by copper assisted coupling of n-$C_8F_{17}I$ and 4-iodophenol. Conducting

the reaction in dimethylsulfoxide (DMSO) resulted in production of some n-$C_7F_{15}C(O)C_6H_4OH$ in addition to the desired product. Only n-$C_8F_{17}C_6H_4OH$ was formed using dimethylformamide (DMF) as solvent.

3.1.3 Phosphate and Phosphonate Synthesis

Two major series of compounds were synthesized, namely phosphates and phosphonates e.g.

$$(3-x)R_fC_6H_4OH + (Cl)_{3-x}P(O)(OC_6H_5)_x \longrightarrow (R_fC_6H_4O)_{3-x}P(O)(OC_6H_5)_x$$

$$(3-x)R_fC_6H_4OH + (Cl)_{3-x}P(O)(C_6H_5)_x \longrightarrow (R_fC_6H_4O)_{3-x}P(O)(C_6H_5)_x$$

The processes were usually conducted in mixed solvents, benzene/Freon-113, in the presence of triethylamine (TEA). All the compounds synthesized, together with relevant data are listed in Table 1. Yields of the products such as:
$[p\text{-}C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)OC_6H_5$ (VII),
$[p\text{-}C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)C_6H_5$ (VIII) and
$[p\text{-}C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]_2P(O)OC_6H_5$ (XVI) where the reaction conditions were to a degree optimized, were of the order of 80%. In the case of the other members of the series, usually only one preparation was carried out to obtain a sufficient sample for screening tests.

3.1.4 Rust Inhibiting Mixtures Synthesis

The rust inhibiting additives were prepared only in mixtures with phosphates and phosphonates. The active factor in these materials is the P-OH moiety. The compounds were obtained

TABLE 1

SUMMARY OF PROPERTY DATA FOR THE PHOSPHATE/PHOSPHONATE ADDITIVES

Compound[a]		Yield %	MP °C	BP[b] °C	H.S.E.[c] %Rec.	TGA[d] Onset °C	TGA[d] $T_{1/2}$ °C	T.D. Volatiles[e] Krytox mg/g	T.D. Volatiles[e] Fomb. mg/g	T.D. Volatiles[e] Demnum mg/g	MW calc.	MW expt.[f]
$R_fP(O)(OPh)_2$	I	75	-	144-146	96	130	223	0.32	0.73		444	480
$R_fP(O)Ph_2$	II	86	69-71	-	79	150	232	0.96			412	440
$(R_f)_2P(O)OPh$	III	88	-	144-146	38	130	227				562	635
$(R_f)_3P(O)$	IV	87	89-90	-	6	135	223				680	750
$R_f'P(O)(OPh)_2$	V	94	-	145[g]	58	150	245	0.21	0.26		826	860
$R_f'P(O)Ph_2$	VI	75	67-70	-	97	150	245	0.26	12.4		794	830
$(R_f')_2P(O)OPh$	VII	79	-	169-170[g]	19	170	267	0.25	52.9	0.16 0.79[j]	1326	1320
$(R_f')_2P(O)Ph$	VIII	79	-	175-180[g]	79	155	253	0.03	176.9	0.16[j]	1310	1300
$R_f''P(O)Ph_2$	IX	45	h	-	99	165	296	0.13	11.6		1126	1100
$(R_f'')_2P(O)Ph$	X	41	-	i	100	203	308	0.13	132.4		1974	1850
$R_f''P(O)(OPh)_2$	XI	74	-	i	99	190	293	0.31	1.21		1158	1100
$R_f'''P(O)(Ph)_2$	XII	63	110-111	-	98	190	280	0.24	0.51		712	740

TABLE 1 (continued)

SUMMARY OF PROPERTY DATA FOR THE PHOSPHATE/PHOSPHONATE ADDITIVES

Compound[a]		Yield %	MP °C	BP[b] °C	H.S.E.[c] %Rec.	TGA[d] Onset °C	TGA[d] $T_{½}$ °C	T.D. Volatiles[e] Krytox mg/g	T.D. Volatiles[e] Fomb. mg/g	T.D. Volatiles[e] Demnum mg/g	MW calcd.	MW expt.[f]
$(R_f'')_2P(O)OPh$	XIII	38	-	i	70	195	304	0.34	4.40		1990	1980
$(R_f''')_2P(O)Ph$	XIV	32	84-85	-	81	180	294				1146	1150
$R_f'''P(O)(OPh)_2$	XV	57	61-62	-	50	160	283				744	750
$(R_f'''')_2P(O)OPh$	XVI	82	-	i	62	180	285	0.07	0.24	0.23[j]	1658	1540
$(R_f'''')_2P(O)Ph$	XVII	53	-	i	93	215	298	0.23	0.10	-	1642	1570
$(R_f')_2P(O)OPh$	VII-AS	-	-	i		150	285			0.48[j]		
$(R_f')_2P(O)Ph$	VIII-AS	-	-	i						1.03[j]		
$(R_f'''')_2P(O)OPh$	XVI-AS	-	-	170-190[g]		190	301	1.21	1.94	0.03 0.42[j]		
$(R_f'''')_2P(O)Ph$	XVII-AS	-	-	i				0.23	25.1	0.20		

TABLE 1 (concluded)

SUMMARY OF PROPERTY DATA FOR THE PHOSPHATE/PHOSPHONATE ADDITIVES

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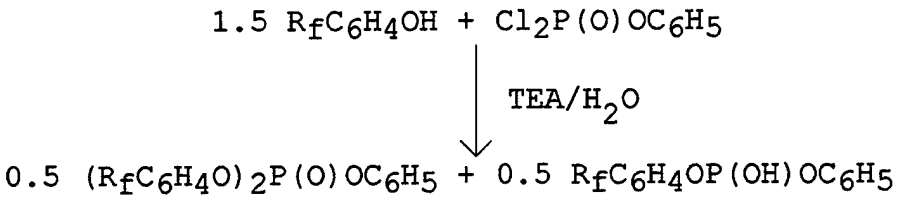
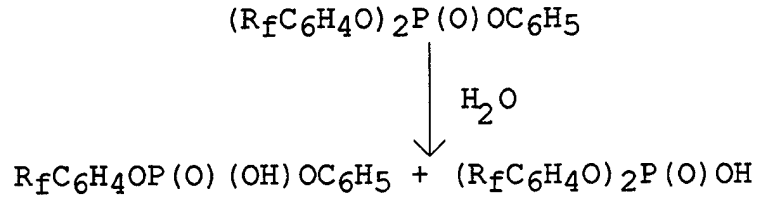
a) $R_f = C_2F_5C_6H_4O$, $R_f' = C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O$, $R_f'' = C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O$, $R_f''' = C_8F_{17}C_6H_4O$, $R_f'''' = C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O$.
b) Boiling point (BP) at 0.001 mm Hg.
c) Hydrolytic stability evaluations were carried out in water at 100°C for 24 h.
d) TGAs were performed at 10°C/min in N_2.
e) Thermal degradation tests were performed in pure oxygen in the presence of M-50 at 316°C over 24 h. Additives were present at 1% (by weight) concentration.
f) Molecular weights of Compounds I-VI were determined in C_6H_6; others in C_6F_6.
g) This is the oil temperature in the micro-distillation apparatus.
h) Compound IX is a waxy solid.
i) The BP was not determined.
j) These tests were performed at 330°C.

either by incomplete substitution followed by water treatment or by hydrolysis of the phosphates and phosphonates i.e.:





In the case of the relatively hydrolytically stable materials (see Section 3.2.2) such as compounds XVI, $[p\text{-}C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]_2P(O)OC_6H_5$ and VIII, $[p\text{-}C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)C_6H_5$, the first process was utilized to prepare the active mixture. In the case of the hydrolytically more labile compounds such as the additive VII, $[p\text{-}C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)OC_6H_5$, the second approach was followed.

To attain a low degree of hydrolysis, the quantity of water was limited. Depending on the amount of the starting material present in the isolated mixture, usually formulation with an additional quantity of the pure phosphate was followed to arrive at 70-90% of the phosphate in the final mixture. This approach was dictated by solubility and the degradation inhibition considerations. It should be noted that the hydrolysis process

gave mainly $R_fC_6H_4OP(O)OC_6H_5(OH)$, based on the predominant formation of $R_fC_6H_4OH$.

The best rust inhibiting additive was the mixture of $[p\text{-}C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]_2P(O)OC_6H_5$ and $p\text{-}C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OP(O)OC_6H_5(OH)$ denoted XVI-AS. Different mixtures containing different proportions of XVI were prepared and their effectiveness tested; these evaluations are fully discussed in Section 3.2.4.

Analogous mixtures based on compounds VII and VIII also exhibited rust inhibiting action, however, the best overall properties were shown by the materials based on the phosphate XVI system.

3.2 ADDITIVE PROPERTY EVALUATIONS

The effectiveness of a given additive as a degradation or rust inhibitor must be associated with solubility in the base fluid and stability in formulation. In actual investigations candidate materials were screened concurrently for effectiveness, solubility and other relevant properties and these results governed the synthesis program. However, for the ease of presentation these different areas are discussed in separate sections.

3.2 1 Volatilities and Solubilities

It is evident from Table 1 compilation that $R_fC_6H_4O$ disubstituted compounds, wherein the R_f groups are

$C_3F_7[OCF(CF_3)CF_2]_{2-4}C_6H_4O$, had weight loss onset above 150°C. Actually, the value for compounds such as $[C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]_2P(O)OC_6H_5$ was ~180°C. For an inhibitor to be effective it must not volatilize at the operational, elevated temperatures. Thus not only the onset temperatures are of importance, but the rates of evaporation, which are reflected in the thermogravimetric analyses traces. The individual graphs are compiled in the experimental section. The T½ values provide some indications as to the rate of evaporation.

It is of interest that the volatilities of the rust inhibiting mixtures are definitely lower than those of the corresponding pure phosphates. This is clearly evident from the comparison graph given in Figure 1. This finding is not surprising, inasmuch as a strongly polar linkage, such as P-OH, promotes association and thus reduction in volatility.

As was discussed earlier, the solubilities of the candidate additives in commercial perfluoropolyalkylether fluids provide important criteria for the final selections. These data are summarized in Table 2. The compilation reveals several aspects, namely the $C_2F_5C_6H_4O$ containing compounds, both mono- and disubstituted, were found to be soluble only at elevated temperatures. It usually required higher temperatures to solubilize the additives in Fomblin Z25 than in Krytox 143AC. Invariably, the phenoxy, OC_6H_5, substituted compounds were soluble at lower temperatures than their C_6H_5 analogues. Compounds having two $C_3F_7[OCF(CF_3)CF_2]_xC_6H_4O$ groups (x = 2,3,4), with the exception

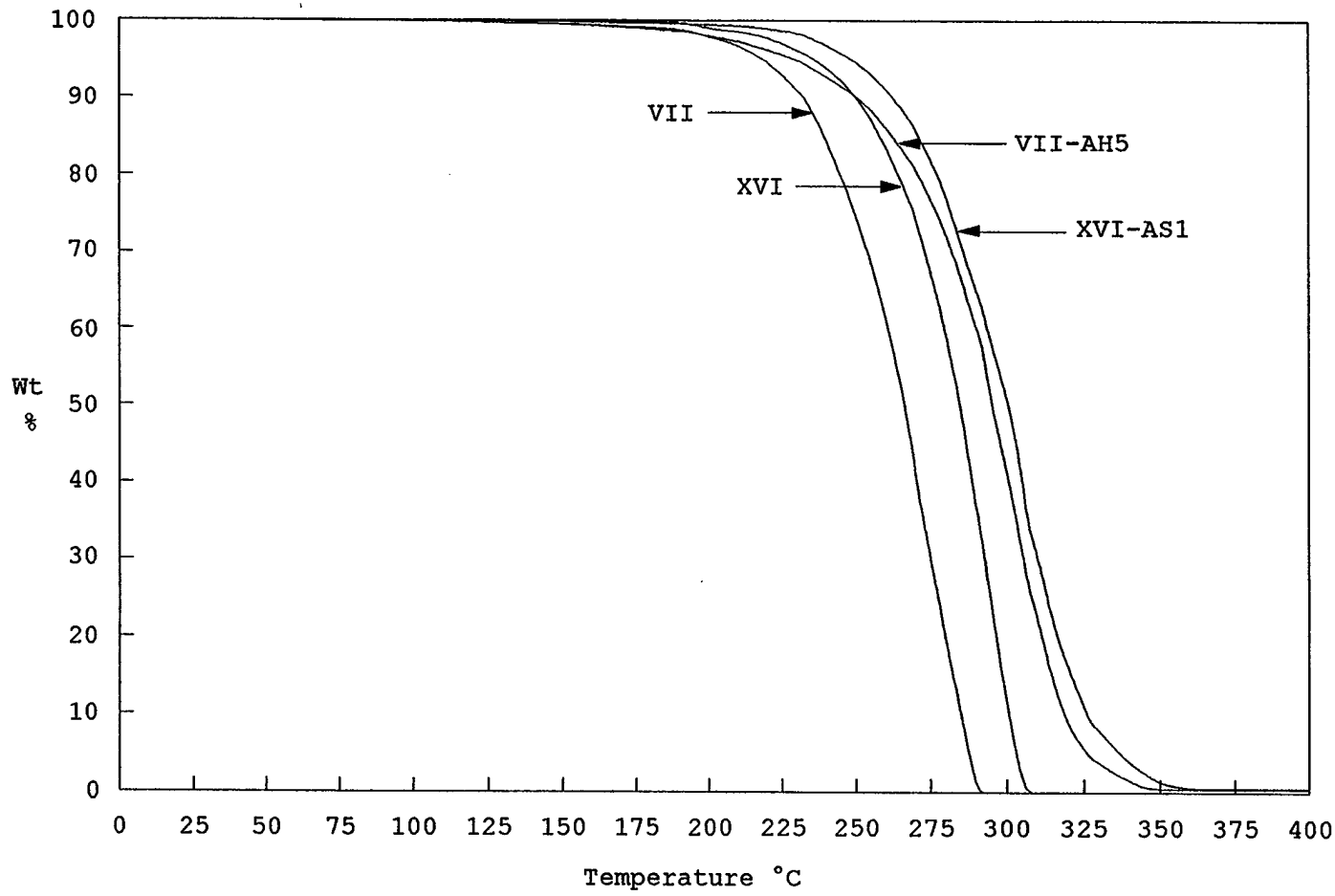


Figure 1. Comparison of the volatility of additives VII, XVI, VII-AH5 and XVI-AS1 as determined by thermal gravimetric analysis (TGA).

TABLE 2

SUMMARY OF SOLUBILITY EVALUATIONS FOR THE ADDITIVES[a]

Additives[b]		Krytox 143AC	Fomblin Z25-P28	Demnum S-100	Brayco MLO 78-80
$(R_f)P(O)(OPh)_2$	I	57	146		
$(R_f)P(O)(Ph)_2$	II	85	172		
$(R_f)_2P(O)(OPh)$	III	65	95		
$(R_f)_3P(O)$	IV	82	77		
$(R_f')P(O)(OPh)_2$	V	95	101	105	68
$(R_f')P(O)(Ph)_2$	VI	106	112		
$(R_f')_2P(O)OPh$	VII	<-40	-8 -30(0.5%)	-40	
$(R_f')_2P(O)Ph$	VIII	<-40	-15[c]	<-40	
$(R_f'')P(O)(Ph)_2$	IX	78	85		52
$(R_f'')_2P(O)Ph$	X	<-40	<-40	<-40	
$(R_f'')P(O)(OPh)_2$	XI	60 41(0.5%) 25(0.2%)	64	65	44
$(R_f''')P(O)(Ph)_2$	XII	115	162		
$(R_f'')_2P(O)OPh$	XIII	<-40	<-40	<-40	
$(R_f''')_2P(O)Ph$	XIV	78	78	81	
$(R_f''')P(O)(OPh)_2$	XV	102	134		
$(R_f'''')_2P(O)OPh$	XVI	<-40	<-40[c]	<-40	
$(R_f'''')_2P(O)Ph$	XVII	<-40	<-40[c]	<-40	

a) 1% by weight additive in fluid, determined by cloud point.
b) $R_f = C_2F_5C_6H_4O$, $R_f' = C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O$,
$R_f'' = C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O$, $R_f''' = C_8F_{17}C_6H_4O$
$R_f'''' = C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O$.
c) Fomblin Z25-P151 was used instead of Fomblin Z25-P28.

of materials where x was 2, were completely soluble in the three commercial fluids down to -40°C. As would be expected, the increase in the length of the perfluoropolyalkylether chain was reflected in a lower solubilization temperature. The $n\text{-}C_8F_{17}C_6H_4O$ substituted materials were soluble only at elevated temperatures, >78°C.

Based on these evaluations, it became apparent that for a practical additive system, only compounds of the general formula $(R_fC_6H_4O)_{3-x}P(O)(OC_6H_5)_x$ or $(R_fC_6H_4O)_{3-x}P(O)(C_6H_5)_x$, wherein x = 0 or 1 and wherein the R_f group is $C_3F_7[OCF(CF_3)CF_2]_{n\geq 2}$ need to be considered. No studies under this program were carried out to determine the minimum length of the perfluoropolyalkylether chain to permit the use of a monosubstituted compounds e.g., $R_fC_6H_4OP(O)(OC_6H_5)_2$. Limited studies of this effect were conducted under a NASA program [Ref. 10] and the results obtained point to feasibility of such an approach. These compounds offer a number of advantages over the disubstituted analogues [Ref. 10].

3.2.2 Hydrolytic Stability

The hydrolytic stability of a given additive is of importance insofar as its "effective" concentration in the fluid is concerned following exposure to moisture and temperature as well as prolonged storage. All the candidate phosphates and phosphonates were subjected to hydrolysis at 100°C. The results of these evaluations are compiled in Table 3. Initially the tests were carried out in benzene; however, subsequent investigations

TABLE 3

100°C HYDROLYTIC STABILITY OF PHOSPHATE/PHOSPHONATE ADDITIVES

Test No.	Compound[a]		Amount mg	Solvent type	Solvent mL	Time h	Recovered Total mg[c]	Recovered S.M.[b] mg	Recovered S.M.[b] %
1	$(R_f)_3P(O)$	IV	246.0	H_2O/C_6H_6	2.5/2.5	17	230.1	230.1	94
2	$(R_f)_3P(O)$	IV	183.0	H_2O	5.0	17	169.3	10.9	6
3	$R_fP(O)Ph_2$	II	255.1	H_2O/C_6H_6	2.5/2.5	16	235.5	235.5	92
4	$R_fP(O)Ph_2$	II	203.6	H_2O	5.0	24	194.5	161.7	79
5	$R_fP(O)(OPh)_2$	I	241.9	H_2O/C_6H_6	2.5/2.5	19	232.0	232.0	96
6	$R_fP(O)(OPh)_2$	I	258.7	H_2O	5.0	18	250.6	250.6	97
7	$R_fP(O)(OPh)_2$	I	271.7	H_2O	5.0	24	261.9	261.9	96
8	$(R_f)_2P(O)OPh$	III	258.2	H_2O	5.0	24	230.7	97.4	38
9	$R_f'P(O)(OPh)_2$	V	252.1	H_2O	5.0	19	237.5	173.2	69
10	$R_f'P(O)(OPh)_2$	V	267.7	H_2O	5.0	24	243.8	155.8	58
11	$R_f'P(O)Ph_2$	VI	237.8	H_2O	5.0	16	237.5	237.5	100
12	$R_f'P(O)Ph_2$	VI	242.1	H_2O	5.0	24	239.1	235.0	97
13	$(R_f')_2P(O)OPh$	VII	256.5	H_2O	5.0	24	220.7	49.6	19
14	$(R_f')_2P(O)Ph$	VIII	218.5	H_2O	5.0	24	212.4	173.0	79
15	$R_f''P(O)Ph_2$	IX	242.7	H_2O	5.0	24	239.5	239.5	99

TABLE 3 (continued)

100°C HYDROLYTIC STABILITY OF PHOSPHATE/PHOSPHONATE ADDITIVES

Test No.	Compound[a]		Amount mg	Solvent type	Solvent mL	Time h	Recovered Total mg[c]	Recovered S.M.[b] mg	Recovered S.M.[b] %
16	$(R_f'')_2P(O)Ph$	X	218.3	H_2O	5.0	24	218.0	218.0	100
18	$R_f''P(O)(OPh)_2$	XI	240.3	H_2O	5.0	24	237.3	237.0	99
19	$R_f'''P(O)Ph_2$	XII	234.0	H_2O	5.0	24	232.9	229.2	98
20	$(R_f'')_2P(O)OPh$	XIII	210.2	H_2O	5.0	24	172.6	146.9	70
21	$(R_f''')_2P(O)Ph$	XIV	235.0	H_2O	5.0	24	221.3	190.3	81
22	$R_f'''P(O)(OPh)_2$	XV	223.3	H_2O	5.0	24	199.3	111.0	50
23	$(R_f'''')_2P(O)OPh$	XVI	233.0	H_2O	5.0	24	227.1	145.3	62
24	$(R_f'''')_2P(O)Ph$	XVII	238.9	H_2O	5.0	24	235.6	221.5	93

a) $R_f = C_2F_5C_6H_4O$, $R_f' = C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O$, $R_f'' = C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O$, $R_f''' = C_8F_{17}C_6H_4O$, $R_f'''' = C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O$.
b) S.M. = Starting Material; % recovery is with respect to the initial quantity of material used.
c) This includes 50, 14, and 25 mg of $C_2F_5C_6H_4OH$ collected in Tests 2, 4, and 8.

revealed that exposure of an additive to water, in the absence of a solvent, provided a more severe environment. This is shown by comparison of Tests 1 and 2 , where in the presence of a solvent $(p\text{-}C_2F_5C_6H_4O)_3P(O)$ recovery (following a 17 hour exposure) was 94%. In the absence of a solvent, the value dropped to 6%. Accordingly, the procedure was standardized to ~250 mg of additive sample, 5 mL of water and a 24 hour exposure at 100°C.

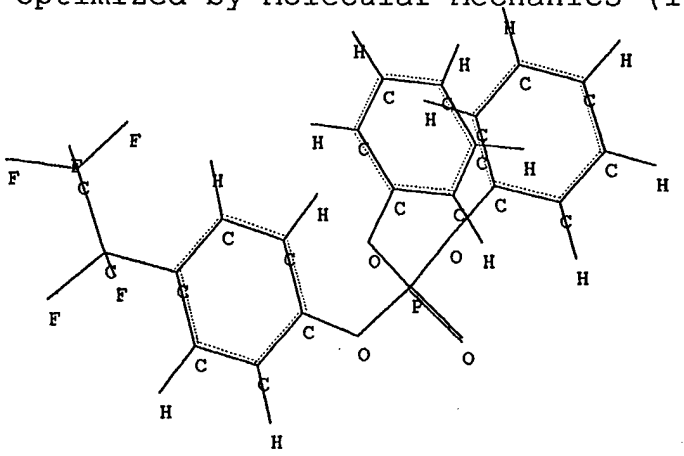
Examining the data listed in Table 3, it is apparent that the presence of a perfluoroalkyl or perfluoroalkylether chain para to the C_6H_4OP linkage promotes ease of hydrolysis. This is reflected in the trend $(R_fC_6H_4O)_3 > (R_fC_6H_4O)_2 > R_fC_6H_4O$. The presence of a phenoxy, as compared to a phenyl substituent, also impairs the hydrolytic stability. This is shown by the quantitative recovery of the starting material in the case of compound X versus only 70% in the case of compound XIII (compare tests 16 and 20, Table 3), as well as the results obtained for compounds XVII and XVI (Tests 24 and 23).

It was noted in Section 3.1.4 that hydrolysis of $(R_fC_6H_4O)_2P(O)(OC_6H_5)$ led mainly to $R_fC_6H_4OP(O)(OC_6H_5)OH$, based on the predominant formation of $R_fC_6H_4OH$. The very limited computational studies of the solvation effect, depicted in Figure 2, seem to support this finding. This is shown by what appears to be a preferential solvation of the $R_fC_6H_4O$-P bond in $p\text{-}C_2F_5C_6H_4OP(O)(OC_6H_5)_2$.

Comparing the hydrolytic stabilities of the phosphates, $(R_fC_6H_4O)_2P(O)OC_6H_5$, specifically compounds VII, XVI and XIII,

$C_2F_5C_6H_4OP(O)(OC_6H_5)_2$

Geometry optimized by Molecular Mechanics (in vacuo)



Geometry optimized by Molecular Mechanics (water solvated)

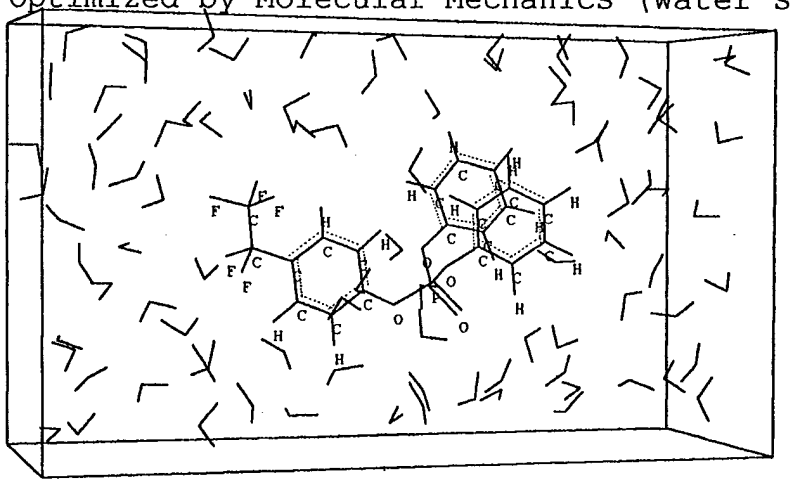


Figure 2. Computational modeling of $C_2F_5C_6H_4OP(O)(OC_6H_5)_2$ solvation aspects.

wherein x in $C_3F_7[OCF(CF_3)CF_2]_x$ increases from 2 to 4, the increase in the length of the perfluoroalkylether chain corresponds to an increase in resistance to hydrolysis. This effect could be due to steric factors or the increasing hydrophobic nature of the molecule; most likely to both.

In the envisioned applications, the additives will not be exposed to potential hydrolysis in a pure state but as a fluid formulation. Thus, it was necessary to determine the hydrolytic stability of the actual formulations. Tests were carried out in Demnum S-100 fluid at 1% additive concentrations using 24 h exposure to water at 100°C. In the case of phosphate VII the additive survival, following the treatment, was 86% (in the absence of the fluid the value was 19%, see Table 3). In the case of phosphate XVI, under the above conditions, no loss of the additive was observed. For the degradation/rust inhibitor, XVI-AS, the phosphate XVI survival was 75%. It must be stressed that hydrolysis, if any, of the phosphates generates in situ the rust inhibiting moiety. Furthermore, the loss of the actual additive, under these rather drastic conditions, is not sufficient to impair the degradation protective action. The different aspects affecting the effectiveness of the additives are discussed in the subsequent section.

3.2.3 Thermal Oxidative Degradation Inhibition

The phosphates and phosphonates were synthesized primarily as thermal oxidative degradation and corrosion

inhibitors and as lubricity additives for perfluoropolyalkylether fluids. Modification of the synthesis procedures led to mixtures containing P-OH moieties, which permitted the use of this family of materials also as rust inhibitors.

To assess the degradation and corrosion arresting action of the candidate materials and to determine which type of compositions offer the best potential, screening studies using the procedure described earlier [Ref 11] were carried out in Krytox 143AC fluid in the presence of M-50 steel. The results of these evaluations are summarized in Figure 3. All the compounds evaluated, with the exception of $C_2F_5C_6H_4P(O)(C_6H_5)_2$ (0.96 mg/g), were found to generate less than 0.5 mg/g of volatiles at 316°C over the 24 h exposure compared to 47.5 mg/g for the fluid alone. Based on the previous studies [Ref. 12] the value of $\leq$0.5 mg/g represents essentially an absence of degradation. An increase in temperature from 316°C to 330°C raised the volatile production just above the acceptable threshold of 0.5 mg/g for VIII (from 0.03 to 0.6 mg/g). For XVI, the volatile production at 330°C was 0.36 mg/g compared to 0.07 mg/g at 316°C.

Additives VII, VII-AH, VIII, XVI and XVI-AS were selected for further studies in Demnum S-100 in the presence of M-50 steel. The selection was governed by solubility, volatility, lubricity [Ref. 13] and rust inhibition considerations. Both VII-AH5 and XVI-AS were effective antirust additives.

The results of the Demnum S-100 studies are summarized in Figure 4. The additives VIII and XVI were fully effective at

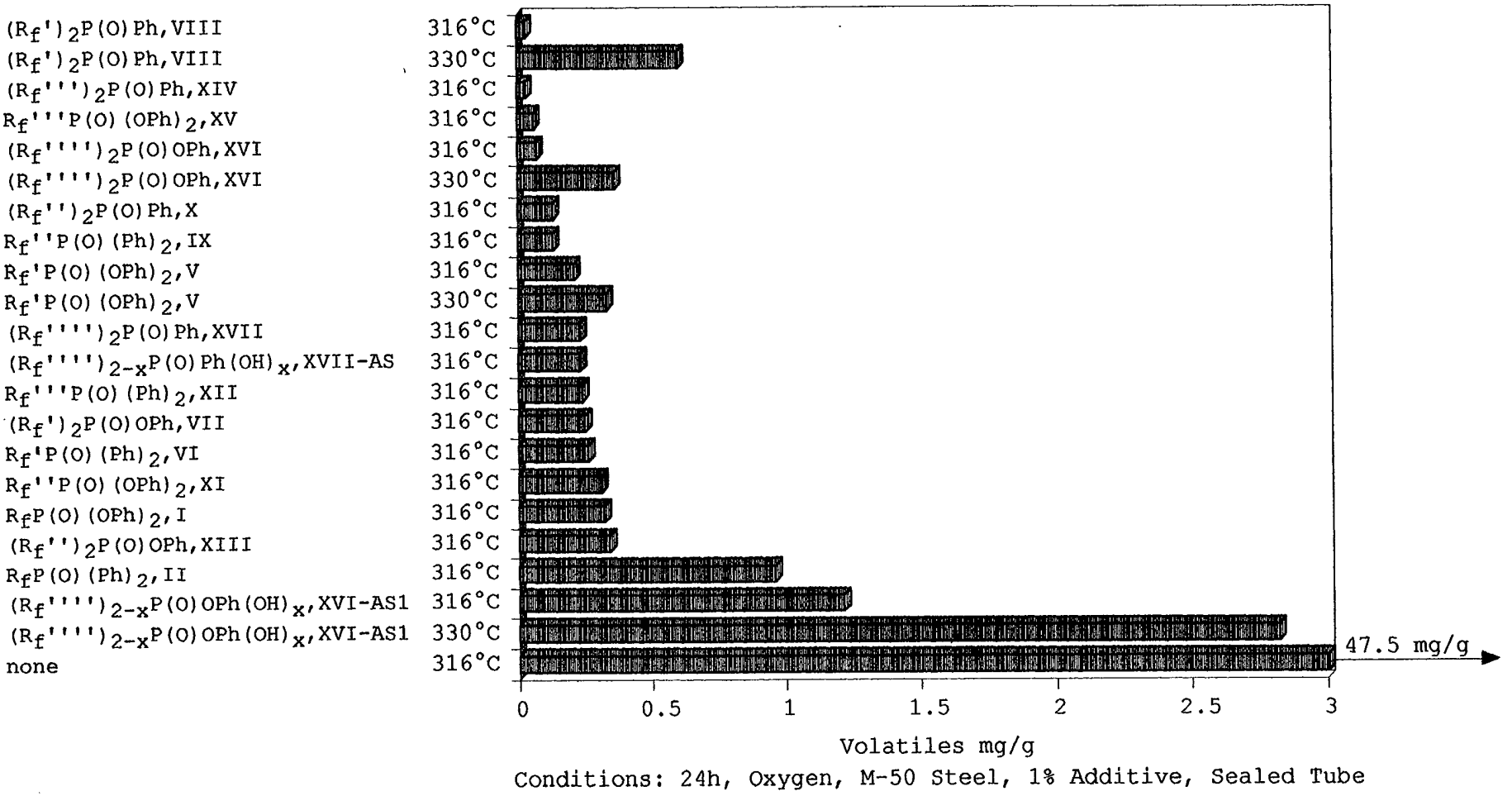


Figure 3. Comparison of effectiveness of different additives in arresting Krytox 143AC thermal oxidative degradation in the presence of M-50 steel over 24 h. (R_f, $C_2F_5C_6H_4O$; R_f', $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O$; R_f'', $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O$; R_f''', $C_8F_{17}C_6H_4O$; R_f'''', $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O$).

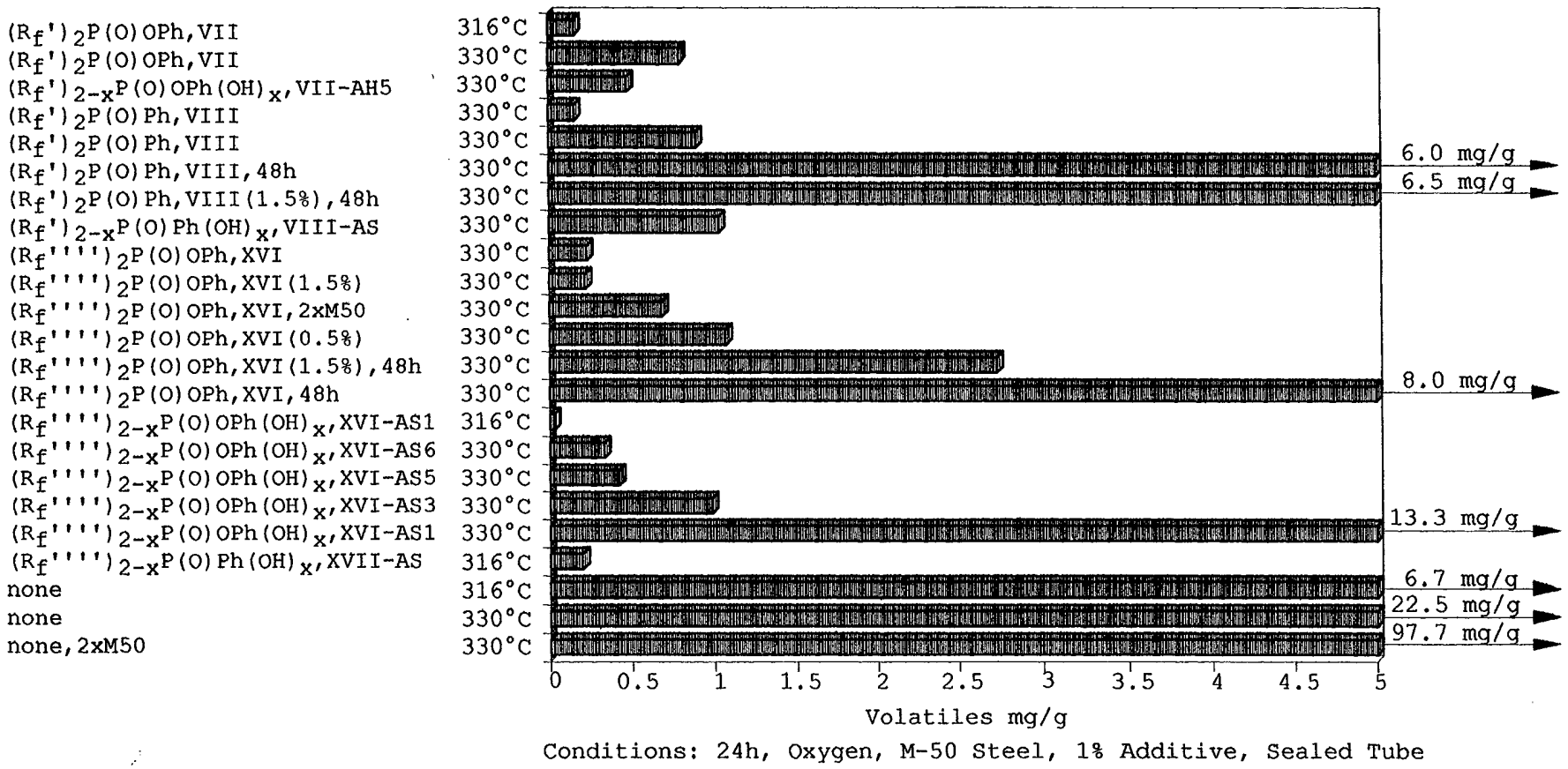


Figure 4. Effectiveness of selected additives in arresting Demnum S-100 thermal oxidative degradation in the presence of M-50 steel. (R_f', $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O$; R_f'''', $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O$).

330°C over the 24 h period, although in a duplicate run of VIII the volatile production was above the 0.5 mg/g threshold.

Pure additive VII, at 330°C over the 24 h exposure, failed to reduce the volatiles production below 0.5 mg/g; however, the 0.79 mg/g value obtained did not exceed the limit significantly. Furthermore, the rust inhibiting mixture, VII-AH5 (VII = 91%), showed degradation arresting action below the threshold limit (0.48 mg/g). It should be noted that the rust inhibiting mixtures XVI-AS5 and XVI-AS6 were fully effective at 330°C over the 24 h exposure. The poor performance of XVI-AS1 and XVI-AS2 is due to low purity; these were early samples before the procedure was well established. The degradation arresting action of VIII-AS was essentially unacceptable (volatiles, 1.03 mg/g); on the other hand in view of its lubricity enhancing characteristics this additive cannot be rejected.

Lengthening the exposure at 330°C to 48 h, in the case of VIII and XVI, resulted in the increase of the degradation extent to 6.0 and 8.0 mg/g, respectively. Reducing the concentration of XVI to 0.5% increased volatiles production, over the 24 h, from 0.23 to 1.07 mg/g. Higher XVI concentration, 1.5%, did not affect the volatiles production over 24 h at 330°C compared to the 1.0% loading (0.23 versus 0.22 mg/g). The higher concentration, however, reduced volatiles production, at 330°C over 48 h, from 8.0 to 2.73 mg/g. In the case of VIII the higher concentration had no effect on the performance over the 48 h exposure.

Doubling the surface area of the M-50 steel, by the use of two coupons, resulted in a more than four fold increase in the amount of degradation products at 330°C over 24 h (from 22.5 to 97 mg/g). The presence of 1% of XVI reduced this value to 0.68 mg/g, which is just above the threshold value of 0.5 mg/g.

The titanium alloy , Ti(6Al,4V), is one of the materials of construction considered for future generation of aircraft; consequently, the effectiveness of additives in inhibiting perfluoropolyalkylether degradation in its presence needed to be assessed. The data for the three most promising candidates, VIII, XVI and the rust preventing mixture of XVI and its diester are given in Figure 5. Although the degree of inhibition (in Demnum S-100 at 330°C over 24 h) was of the order of 3×10^2 for the three materials as compared to the fluid alone (396 mg/g), the result for VIII (1.31 mg/g) was above the 0.5 mg/g limit. Additive XVI was also tested in Krytox 143AC in the presence of Ti(6Al,4V) at 316°C over 24 h; it was fully effective in reducing the volatiles production from 299 to 0.40 mg/g.

Only XVI was evaluated in Demnum S-100 in the presence of Pyrowear 675 stainless steel, a potential replacement of M-50 alloy. The values obtained at 330°C for the first and the second consecutive 24 h exposures, 0.42 and 0.52 mg/g respectively, were below the designated threshold of 0.5 mg/g. It should be stressed that the surface area of Pyrowear 675 ball, 9.58 cm^2, is significantly larger than that of the M-50 coupon, 1.67 cm^2. Furthermore, the additional 24 h exposure did not result in an

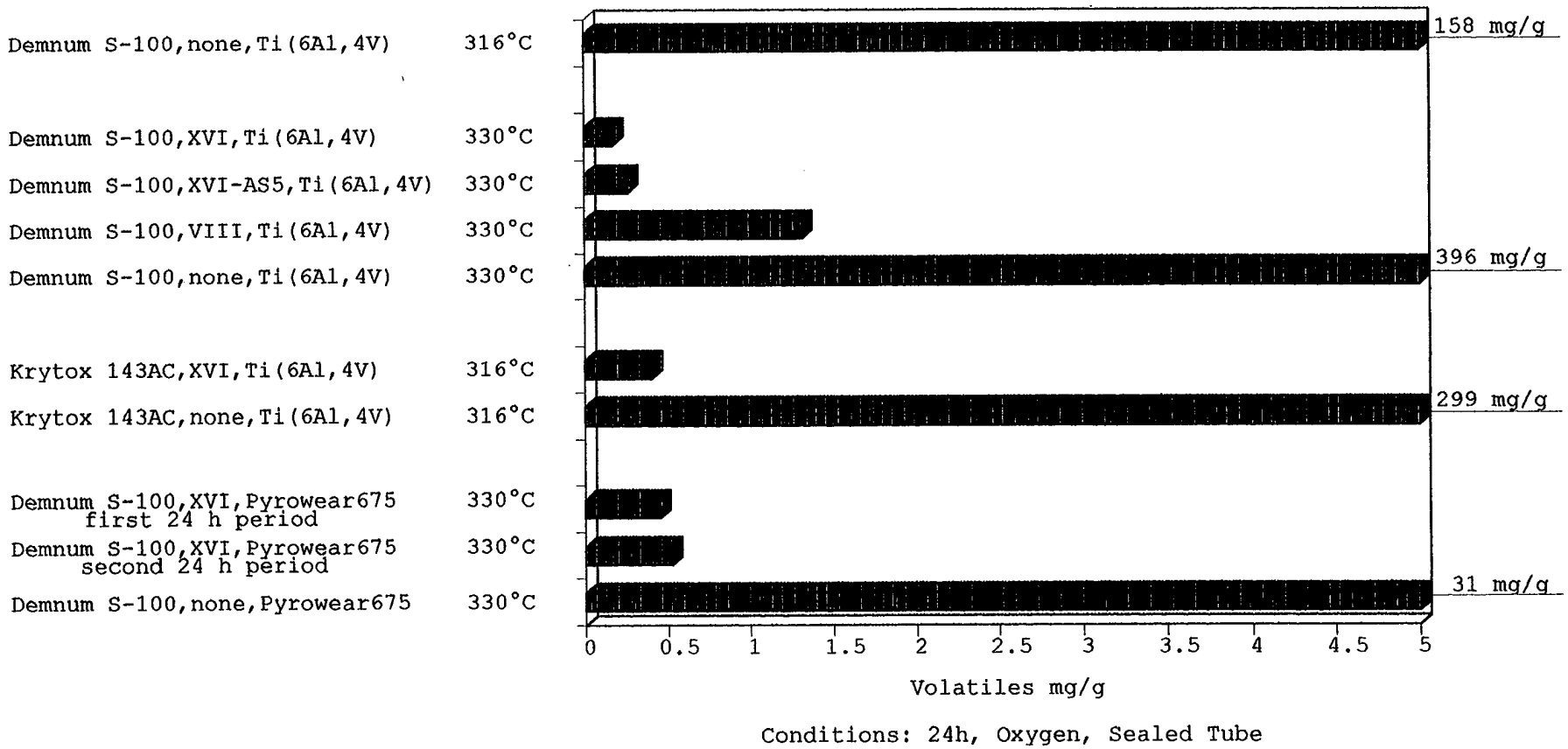


Figure 5. Comparison of effectiveness of selected additives in arresting Demnum S-100 and Krytox thermal oxidative degradation in the presence of Ti(6Al,4V) alloy and Pyrowear 675 steel. (VIII, $(C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O)_2P(O)Ph$; XVI, $(C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O)_2P(O)OPh$; XVI-AS5, $(C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O)_{2-x}P(O)OPh(OH)_x$).

increase of degradation rate. These data, in conjunction with the action of Pyrowear 675 on Demnum S-100 in the absence of an additive, indicate that Pyrowear 675 is less detrimental than M-50 to perfluoropolyalkylether fluids and also more responsive to inhibition.

Past investigations [Ref. 2, 4, 12] showed clearly that the Fomblin Z family of fluids, $-(CF_2O)_x(CF_2CF_2O)_y-$, possess the best viscosity/temperature profiles. Unfortunately, this is associated with the lowest thermal oxidative stability in the presence of metals of all the known perfluoropolyalkylethers fluids. The latter characteristic is illustrated by the formation of 337 and 487 mg/g of degradation products by the two Fomblin Z25 batches, P78 and P151, respectively, on exposure to M-50 in oxygen over 8 h at 316°C. Examining the data presented in Figure 6, it is apparent that in the case of the Fomblin Z25-P28 batch the additives having only one of the phenoxy groups substituted by a perfluoroalkyl or a perfluoroalkylether group were most effective at 316°C: V, 0.26 mg/g; I, 0.73 mg/g; XI, 1.21 mg/g. At 330°C, the best of the series, additive V, limited the volatiles production only to 33 mg/g. Reducing the temperature to 325°C still resulted in an unacceptable value of 11.9 mg/g.

In the Fomblin Z25-P151 batch additives XVII, and XVI, which are disubstituted by a perfluoroalkyletherphenoxy groups, were found to be fully effective at 316°C over the 24 h exposure. Although the current studies do not permit direct comparisons between the additive responsiveness of the two fluid batches, the

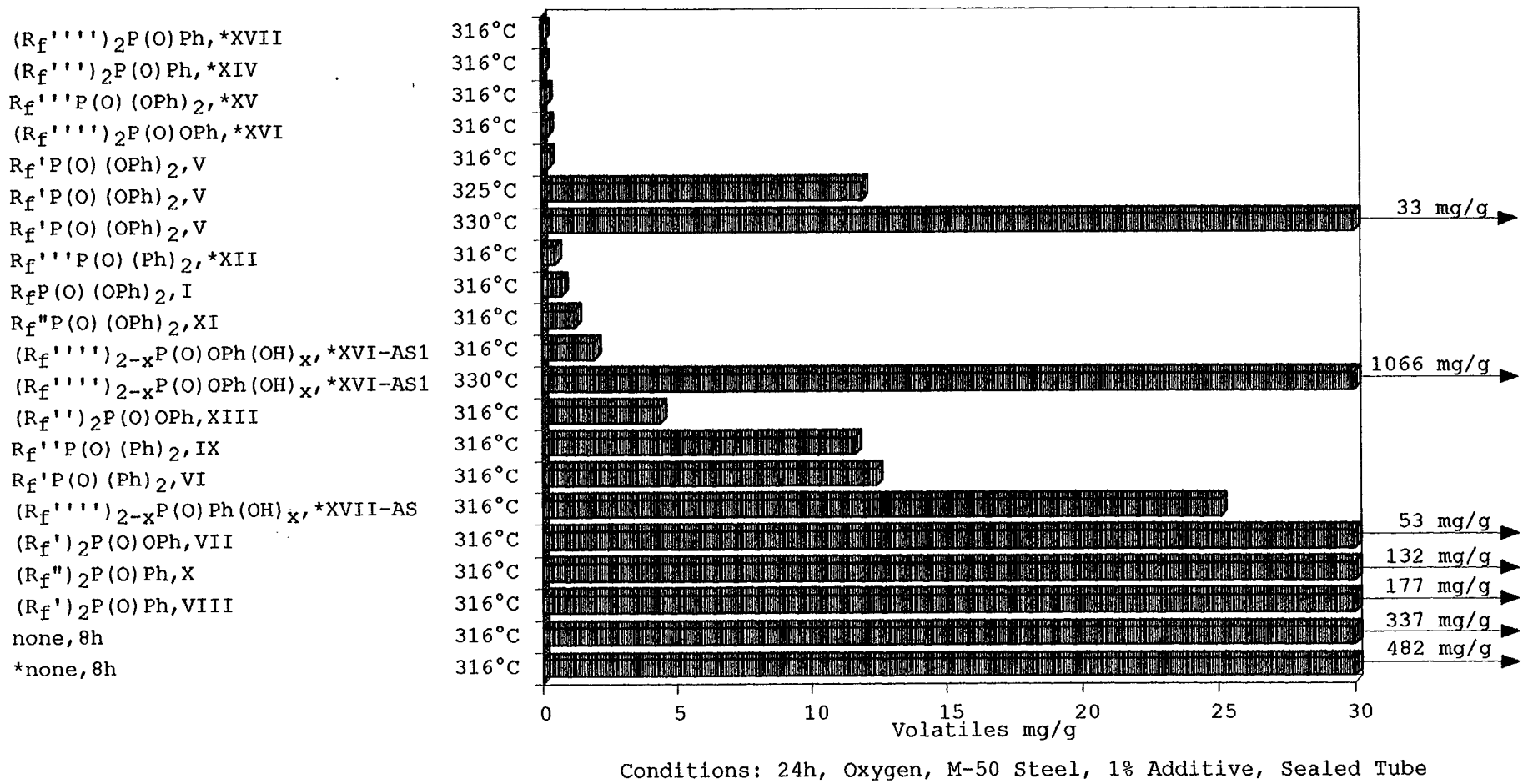


Figure 6. Comparison of effectiveness of selected additives in arresting Fomblin Z25-P28 (* - Fomblin Z25-P151) thermal oxidative degradation in the presence of M-50 steel over 24 h. (R_f, $C_2F_5C_6H_4O$; R_f', $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O$; R_f'', $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O$; R_f''', $C_8F_{17}C_6H_4O$; R_f'''', $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O$).

work performed under the NASA program indicates P151 to be significantly more responsive to additive degradation inhibition [Ref. 10]. It is believed that the lower OCF_2/OCF_2CF_2 ratio, in the latter batch, is responsible for this behavior. Based on the results presented, additive XVI is definitely effective in Fomblin Z25 at 316°C; the rust inhibiting mixture, XVI-AS, gave a value (1.94 mg/g) above the accepted threshold of 0.5 mg/g. However, this was an initially prepared material. It is obvious from the data discussed earlier in this section, that the purer rust inhibiting mixtures, such as XVI-AS5 or XVI-AS6, would be expected to exhibit an action comparable to that of XVI.

To summarize, of the commercial fluids tested, Demnum appeared to offer the best compromise with respect to viscosity/temperature profile and responsiveness to additives. Of the additives tested, phosphate XVI, $[C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]_2P(O)(OC_6H_5)$, or actually its mixture with $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OP(O)(OH)OC_6H_5$ provide the best overall formulation package for rust protection and degradation/corrosion inhibition up to 330°C in the presence of both ferrous and titanium alloys. It is of interest that substitution of the phenoxy group by the tetrameter chain $C_3F_7[OCF(CF_3)CF_2]_3-$, results in improved hydrolytic stability compared to the trimer analogue and better thermal oxidative degradation inhibition than the pentamer system. However, the best lubricity enhancement [Ref. 13] was shown by the Air Force to be the phosphonate, $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)C_6H_5$ (VIII).

3.2.4 Rust Inhibition

The processes utilized in the syntheses of the rust inhibiting mixtures of phosphates and phosphonates were fully discussed in Section 3.1.4. The evaluations were carried out using the optimized Corrosion Resistance Evaluation Procedure (CREP) described previously [Ref. 14].

All the phosphates and phosphonates synthesized under this program were tested for rust preventing action. None of the pure compounds were active; actually, their presence in some instances increased the degree of corrosion. These tests, together with the evaluations performed using the active mixtures and including the controls, are summarized in the Experimental Section. Table 4, included here, lists only the tests carried out on the specifically prepared rust preventing additives.

Figure 7 illustrates the general appearance of coupons after undergoing the CREP test. Brayco 814Z was used as a control, since this fluid did provide some metal protection. The coupon in the absence of any fluid exposure was found to be as extensively corroded, after the test, as the coupon treated with perfluoropolyalkylether fluid, e.g., Krytox 143AC. The extents of corrosion exhibited by an untreated coupon and by coupons exposed to the various perfluoropolyalkylether fluids and then to CREP evaluations, are listed in Table 5.

Coupons ranked 10, following CREP tests, showed no trace of corrosion. The metal surfaces were just as clean and shiny

TABLE4

RESULTS OF CREP TEST EVALUATIONS IN PERFLUOROPOLYALKYLETHER FLUIDS OF PHOSPHATE/PHOSPHONATE ADDITIVES CONTAINING P(OH) GROUP COMPONENTS

Test No.	Fluid	Additive Type[a]		Wt.%	Wt. Change mg	A%/B%	Ranking[b]
1(647)	Demnum S-100	$(R_f')_2P(O)OPh$ (VII, 32%)	VII-AH2	0.5	0.0	0/0	10
2(548)	Krytox 143AC	$(R_f')_2P(O)OPh$ (VII, 59%)	VII-AH1	0.5	0.0	0/0	10
3(572	Demnum S-100	$(R_f')_2P(O)OPh$ (VII, 64%)	VII-AS	0.5	+0.5	0/0	10
4(539)	Krytox 143AC	$(R_f')_2P(O)OPh$ (VII, 66%)	VII-AS	0.5	+0.3	0/0	10
5(560)	Fomblin Z25-P151	$(R_f')_2P(O)OPh$ (VII, 66%)	VII-AS	0.5	+0.6	1/0	9+
6(650)	Demnum S-100	$(R_f')_2P(O)OPh$ (VII, 77%)	VII-AH3	0.5	0.0	0/0	10
7(656)	Demnum S-100	$(R_f')_2P(O)OPh$ (VII, 86%)	VII-AH4	0.5	+0.1	0/0	10
8(659)	Demnum S-100	$(R_f')_2P(O)OPh$ (VII, 91%)	VII-AH5	0.5	0.0	0/0	10
9(662)	Demnum S-100	$(R_f')_2P(O)OPh$ (VII, 91%)	VII-AH5	0.5	0.0	0/0	10(24h)
10(701	Demnum S-100	$(R_f')_2P(O)OPh$ (VII, 91%; 6 months test)	VII-AH5	0.5	+0.1	0/0	10(24h)
11(644)	Demnum S-100	$(R_f')_2P(O)OPh$ (VII, 95%)	VII-AH2	0.5	0.0	0/0	10
12(668)	Demnum S-100	$(R_f')_2P(O)Ph$ (VIII, 62%)	VIII-AS	0.5	+0.1	1/1	9+

TABLE 4 (Continued)

RESULTS OF CREP TEST EVALUATIONS IN PERFLUOROPOLYALKYLETHER FLUIDS OF PHOSPHATE/PHOSPHONATE ADDITIVES CONTAINING P(OH) GROUP COMPONENTS

Test No.	Fluid	Additive Type[a]	Wt.%	Wt. Change mg	A%/B%	Ranking[b]
13(677)	Demnum S-100	$(R_f')_2P(O)Ph$ VIII-AS (VIII, 62%)	1.0	+0.1	1/1	9+
14(680)	Demnum S-100	$(R_f')_2P(O)Ph$ VIII-AS (VIII, 62%)	1.0	0.0	1/1	9+(24h)
15(653)	Demnum S-100	$(R_f')_2P(O)Ph$ VIII-AH (VIII, 82%)	0.5	+0.1	3/2	9
16(554)	Demnum S-100	$(R_f'''')_2P(O)OPh$ XVI-AS1 (XVI, 61%)	0.5	0.0	0/0	10
17(542)	Krytox 143AC	$(R_f'''')_2P(O)OPh$ XVI-AS1 (XVI, 61%)	0.5	+0.4	0/0	10
18(569)	Krytox 143AC	$(R_f'''')_2P(O)OPh$ XVI-AS1 (XVI, 61%)	0.5	+0.4	0/0	10(24h)
19(551)	Fomblin Z25-P151	$(R_f'''')_2P(O)OPh$ XVI-AS1 (XVI, 61%)	0.5	0.0	0/0	10
20(545)	Krytox 143AC	$(R_f'''')_2P(O)OPh$ XVI-AH (XVI, 64%)	0.5	0.0	0/0	10
21(581)	Krytox 143AC	$(R_f'''')_2P(O)OPh$ XVI-AS2 (XVI, 81%)	0.5	+0.7	0/0	10
22(587)	Demnum S-100	$(R_f'''')_2P(O)OPh$ XVI-AS2 (XVI, 81%)	0.5	+0.1	0/1	9+(24h)
23(623)	Demnum S-100	$(R_f'''')_2P(O)OPh$ XVI-AS2A (XVI, 94%)	0.5	+0.4	0/0	10

TABLE 4 (Continued)

RESULTS OF CREP TEST EVALUATIONS IN PERFLUOROPOLYALKYLETHER FLUIDS OF PHOSPHATE/PHOSPHONATE ADDITIVES CONTAINING P(OH) GROUP COMPONENTS

Test No.	Fluid	Additive Type[a]	Wt.%	Wt. Change mg	A%/B%	Ranking[b]
24(590)	Demnum S-100	$(R_f'''')_2P(O)OPh$ XVI-AS3 (50/50 mix XVI-AS2/XVI; XVI 90%)	0.5	+0.6	0/0	10
25(665)	Demnum S-100	$(R_f'''')_2P(O)OPh$ XVI-AS5 (XVI, 85%)	0.5	+0.1	0/0	10
26(674)	Demnum S-100	$(R_f'''')_2P(O)OPh$ XVI-AS5 (XVI, 85%)	0.5	0.0	0/0	10(24h)
27(683)	Demnum S-100	$(R_f'''')_2P(O)OPh$ XVI-AS5 (XVI, 85%; 6 months test)	0.5	0.0	0/0	10(24h)
28(686)	Krytox 143AC	$(R_f'''')_2P(O)OPh$ XVI-AS5 (XVI, 85%; 6 months test)	0.5	+0.1	0/0	10(24h)
29(695)	Demnum S-100	$(R_f'''')_2P(O)OPh$ XVI-AS6A (XVI, 87%)	0.5	0.0	0/0	10
30(692)	Demnum S-100	$(R_f'''')_2P(O)OPh$ XVI-AS6B (XVI, 93%)	0.5	0.0	0/0	10
31(722)	Demnum S-100	$(R_f'''')_2P(O)OPh$ XVI-AS6AB (XVI, 86%)	0.5	0.1	0/0	10(24h)
32(706)	Krytox 143AC	$(R_f'''')_2P(O)OPh$ XVI-AS6A (XVI, 87%)	0.1	0.1	1/0	9+
33(708)	Demnum S-100	$(R_f'''')_2P(O)OPh$ XVI-AS6A (XVI, 87%)	0.1	0.0	1/1	9+
34(626)	Demnum S-100	$(R_f'''')_2P(O)Ph$ XVII-AS (XVII, 72%)	1.5	0.0	25/30	4

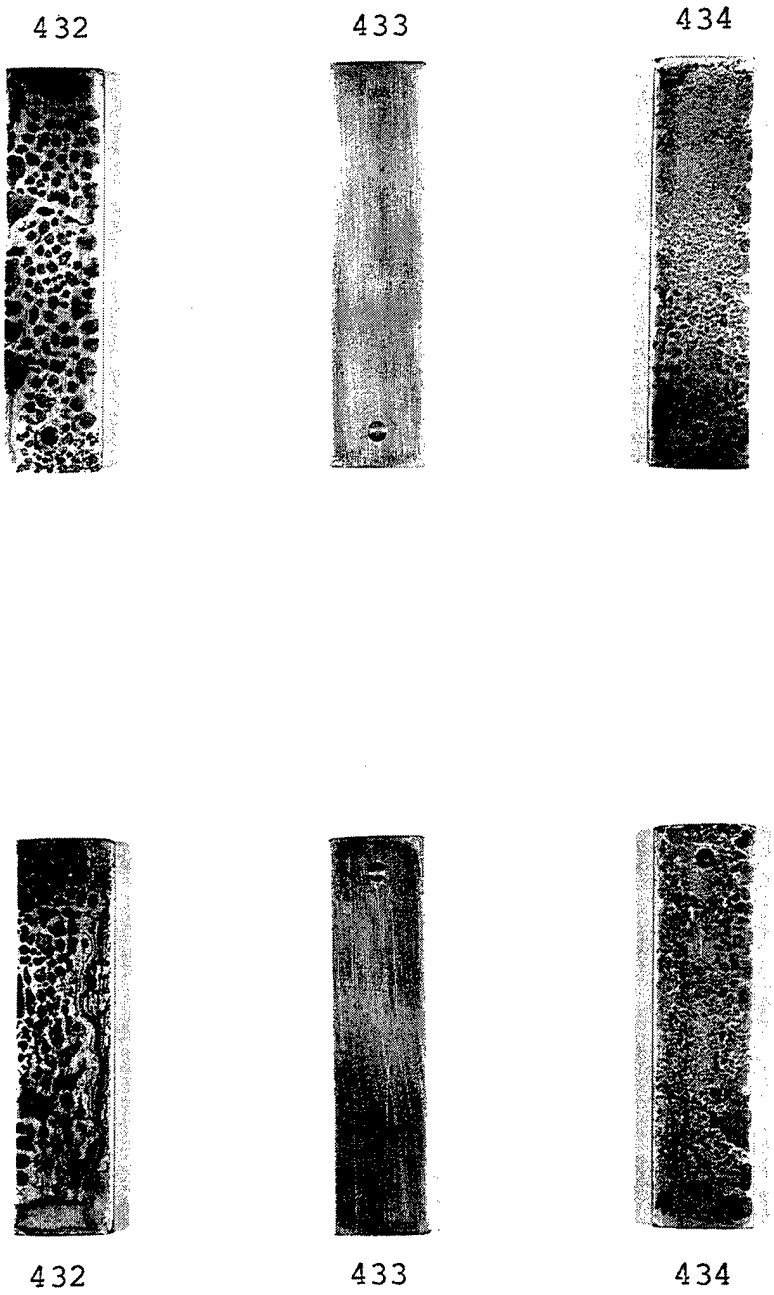
TABLE 4 (Continued)

RESULTS OF CREP TEST EVALUATIONS IN PERFLUOROPOLYALKYLETHER FLUIDS OF PHOSPHATE/PHOSPHONATE ADDITIVES CONTAINING P(OH) GROUP COMPONENTS

Test No.	Fluid	Additive Type[a]	Wt.%	Wt. Change mg	A%/B%	Ranking[b]
35(596)	Demnum S-100	$(R_f'''')_2P(O)Ph$ XVII-AS (XVII, 72%)	0.5	+0.7	15/20	5
36(614)	Demnum S-100	$(R_f'''')_2P(O)Ph$ XVII-AS (XVII, 72%)	1.5	0.0	20/15	7
37(608)	Demnum S-100	$(R_f'''')_2P(O)Ph$ XVII-AS (XVII, 98%)	0.5	-1.4	85/75	-4
38(575)	Krytox 143AC	$(R_f'''')_2P(O)Ph$ XVII-AS (XVII, 98%)	0.5	-0.1	5/20	6
39(578)	Fomblin Z25-P151	$(R_f'''')_2P(O)Ph$ XVII-AS (XVII, 98%)	0.5	-1.7	70/80	-7

a) $R_f' = C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O$, $R_f'''' = C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O$. The "active" compounds $R_fP(O)(OR)OH$ and $R_fP(O)(R)OH$ were introduced either by reagents stoichiometry in the synthesis or by hydrolysis of $(R_f)_2P(O)OR$ or $(R_f)_2P(O)R$ compounds. The synthesized series is denoted AS, the hydrolyzed series by AH. Unless denoted otherwise tests were conducted over 1 h period.

b) Rankings are made on a scale of 0 to 10 with 0 representing a corroded coupon corresponding to a blank (fluid alone), 10 representing total absence of corrosion and 9+ corresponding to a coupon with corrosion lower than 5% of the blank. Negative values are given when the corrosion using the formulated fluid was more extensive than that of the blank.



Untreated	Brayco 814Z	Krytox 143AC
(-0.3 mg)	(-0.1 mg)	(-1.6 mg)

Figure 7. Coupons from CREP evaluations of Brayco 814Z and Krytox 143AC fluids.

TABLE 5

CREP TEST EVALUATIONS (1 h TEST)

Test No.	Fluid	Wt. Loss mg.	A%/B%[a]
432	Untreated	0.3	70/80
433	Brayco 814Z	0.1	0/1
434	Krytox 143AC	1.6	80/80
438	Demnum S-100	1.0	80/85
439	Demnum S-20	0.9	75/80
440	Fomblin Z25 P28	1.2	75/80

a) A and B refer to the two sides of the coupon. The numbers represent the percent of the surface which had been attacked.

after the CREP as prior to the test. The data presented in Table 4 show clearly that a range of compositions comprising from 32% up to 95% of additive VII, with just one exception, prevented corrosion totally. The effectiveness of rust inhibition persisted over a 24 h exposure.

The potential rust inhibiting mixtures based on the phosphonate VIII, $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)C_6H_5$, were less effective. The best ranking obtained was 9^+. Increasing additive concentration to 1% failed to improve the performance. On the other hand, extending the exposure to 24 h did not result in more extensive corrosion.

All the rust inhibiting mixtures of XVI, ranging from 61 to 94% of XVI, exhibited complete corrosion prevention at 0.5% loading in both the 1 hour and 24 hour tests. Even at 0.1% concentration the 87% mixture had a CREP of 9^+. Mixtures derived from the corresponding phosphonate, $[C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]_2P(O)C_6H_5$ (XVII), containing from 72 to 98% of XVII, at best showed marginal protection, at worst (at 98% of XVII) could be viewed as corrosion promoters with CREP as low as -7. Increase of the concentration to 1.5% failed to improve performance. Apparently, the presence of a phenoxy versus a phenyl group promotes the corrosion inhibiting characteristics. The greater polarity of the P-O bond compared to the P-C linkage is most likely responsible for the observed behavior. This effect is not so pronounced in the trimer-substituted analogue, VIII, most likely the hydrophobic influence of the longer chain in

conjuction with the attendant steric shielding also plays a role. These results show clearly that for the best action a number of different factors need to be perfectly balanced. The optimum structural arrangement can be identified only experimentally.

3.2.5 Shelf Life Stability

The most promising additives, both for thermal oxidative degradation inhibition and rust prevention, were evaluated for performance and solution stability at the standard formulation concentrations in Demnum S-100 over a period of 6 months. During that time, the solution appearance was monitored. At the end of the 6 months exposure, the formulated fluids were tested and the results compared with the data obtained for the freshly made samples. The results are summarized in Table 6 and fully described in the Experimental Section.

TABLE 6

SHELF LIFE ADDITIVE EFFECTIVENESS EVALUATIONS IN DEMNUM S-100

Additive	Concentration %	T. D. 24 h, 330°C Fresh mg/g	T. D. 24 h, 330°C Aged mg/g	CREP 24 h Ranking Fresh	CREP 24 h Ranking Aged
VII	1	0.16	0.33		
XVI	1	0.27	0.39		
VII-AH5	1	0.48	0.38		
XVI-AS5	1	0.42	0.36		
VII-AH5	0.5			10	10
VII-AH5	0.5 (in Krytox)			10	10
XVI-AS5	0.5			10	10

The shelf life stability evaluations concluded the investigations carried out on the development of novel thermal oxidative degradation, rust inhibiting and lubricity enhancing additives. This research resulted in production of materials which are relatively involatile, soluble down to -40°C, stable in storage, rust preventing and functioning as degradation/corrosion inhibitors in Demnum fluids up to 330°C in the presence of ferrous and titanium alloys. Samples, approximately 30 g, of the most promising additives were delivered for further evaluations by WL/MLBT, Wright Laboratory.

4. EXPERIMENTAL

General

All solvents used were reagent grade and were dried and distilled prior to use. Operations involving moisture or air sensitive materials were carried out either in an inert atmosphere enclosure (Vacuum Atmospheres Model HE-93BO) under nitrogen bypass or using vacuum line techniques. The commercially available starting materials were usually purified by distillation, crystallization, or other appropriate means.

All melting points are uncorrected and were determined in evacuated sealed capillaries. Infrared spectra were recorded as gas spectra, neat (on liquids) and as double mulls (Kel-F oil No. 10 and Nujol) on solids using a Perkin-Elmer Corporation infrared spectrophotometer Model 1330. The mass spectrometric (MS) analyses were obtained employing a Du Pont 21-491B double focusing mass spectrometer attached to a Varian Aerograph Model 2700 gas chromatograph, equipped with a flame ionization detector and a Du Pont 21-094 data acquisition and processing system. The majority of product mixture identifications were performed using combined gas chromatography/mass spectrometry (GC/MS). Gas chromatography (GC) was conducted employing a 10 ft x 1/8 in stainless steel column packed with 4% OV-101 on 80/100 mesh Chromosorb G or a 3 ft x 1/8 in stainless steel column packed with 3% Dexsil 300 on 100/120 mesh Chromosorb WAW, using a programming rate of 8°C/minute from 50-300°C. Molecular weights were determined in

hexafluorobenzene using a Mechrolab Model 302 vapor pressure osmometer. Thermal gravimetric analyses (TGA) were carried out in nitrogen at 10°C/min.

Materials

Poly(hexafluoropropene oxide) fluid, $F[CF(CF_3)CF_2O]_nC_2F_5$, (Krytox 143AC product of Du Pont) was obtained from the Air Force (MLO 71-6); the linear fluid, $-[CF_2CF_2CF_2O]_n-$, was received from Daikin Co. (Demnum S-20 and S-100). Two batches of Fomblin Z25, P-28 and P-151 were studied; both were received from Ausimont USA, Inc.

Degradation

All the tests were carried out in pure oxygen (~400 mm Hg pressure at 25°C) in the presence of M-50, Pyrowear 675 and Ti(6Al,4V) alloys over 24 h or other specified periods at the denoted temperatures. At the end of exposure the volatile condensables were removed in vacuo and weighed. Detailed description of the procedure and apparatus was reported previously [Ref. 11].

Preparation of $p\text{-}CF_3C(O)C_6H_4Br$

To p-dibromobenzene (113 g, 478 mmol) in ether (400 mL) cooled to -5°C (bath) was added n-butyllithium (200 mL, 2.5 M in hexanes 0.5 mol) over a period of 1 h. The reaction mixture was subsequently stirred at -5° to -7°C for additional 1 h. The

cooling bath was then replaced with a Dry Ice-acetone bath and ethyltrifluoroacetate (66.0 g, 46.5 mmol) was added over a period of 35 minutes. Stirring was continued for 2 h at -78°C. The reaction mixture was poured onto cold hydrochloric acid (300 mL, 2 N). The organic layer was separated and combined with the ether (50 mL) extract of the aqueous layer, washed with water (4 x 60 mL) and dried over anhydrous magnesium sulfate. Following solvent removal under reduced pressure, the product, 103 g (85% yield, GC purity 95%), was purified by distillation to give 91.1 g (75% yield), BP 99-100°C/26 mm Hg, of $CF_3C(O)C_6H_4Br$ (GC purity 98%). The infrared spectrum is given in Figure 8, the mass spectrum in Table 7.

Preparation of $C_2F_5C_6H_4Br$

A stainless steel Parr pressure reactor (600 mL) was charged with $CF_3C(O)C_6H_4Br$ (90.6 g, 358 mmol), Freon-113 (150 mL) followed by anhydrous HF (45 mL). It should be noted that the reactor was cooled briefly with Dry Ice under nitrogen atmosphere before the anhydrous HF was poured in and the reactor was immediately closed. Sulfur tetrafluoride (89 g, 824 mmol), pre measured in a storage cylinder, was transferred into the reactor (cooled in a Dry Ice bath) via pressure hose. Subsequently, the reactor was heated in a sand bath at 110°C for 16 h while agitated using a mechanical shaker. Following cooling to room temperature and venting, the contents were poured into ice water (200 mL); the reactor was washed with Freon-113 (70 mL) and the washings

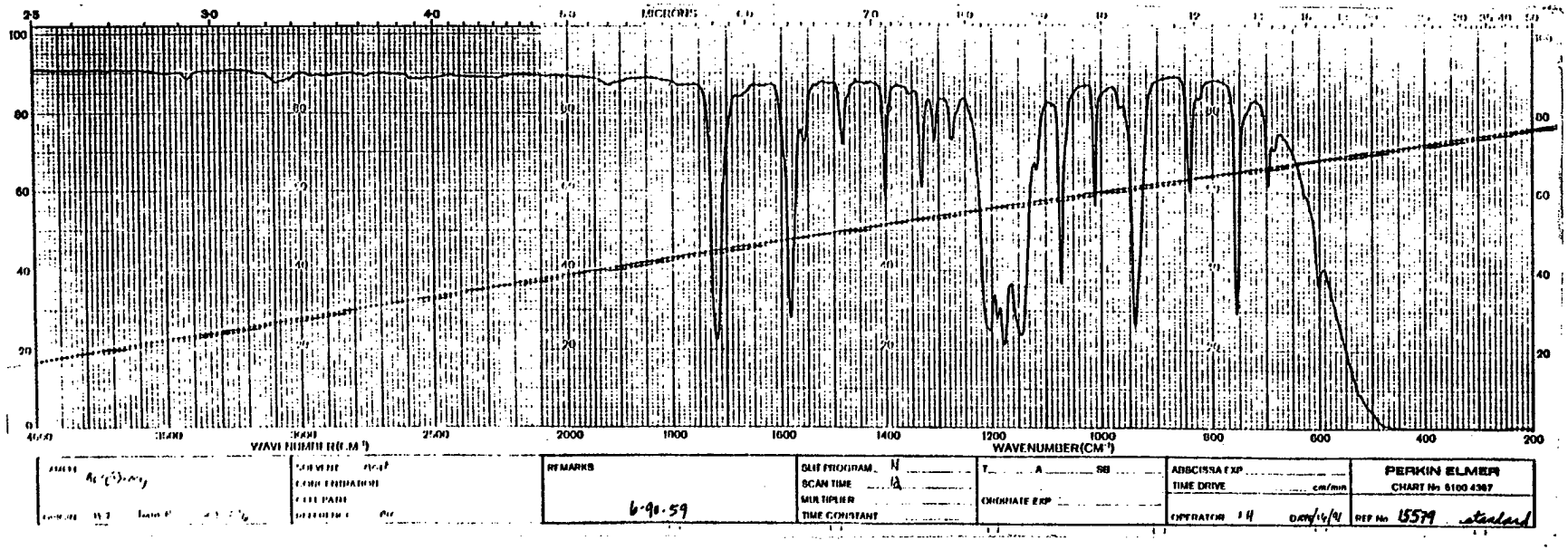


Figure 8. Infrared spectrum of $BrC_6H_4COCF_3$.

TABLE 7

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF

$CF_3C(O)C_6H_4Br$ (MW 252)

m/e	%	m/e	%	m/e	%	m/e	%
20	3.8	69	24.2	94	7.2	158	15.3
26	6.0	73	18.3	95	10.4	173	4.2
27	3.7	74	46.9	103	4.4	174	3.8
28	8.2	75	67.0	104	21.1	175	3.7
31	7.3	76	70.0	105	12.0	183	100.0
36	3.7	77	26.7	106	3.2	184	24.8
37	16.6	78	11.1	107	5.9	185	96.9
38	26.4	79	10.0	123	6.6	187	3.4
39	7.8	80	11.1	129	7.2	221	3.2
49	14.0	81	10.0	130	3.5	249	3.2
50	69.6	82	10.0	131	9.3	252	58.6M^+
51	21.9	85	3.0	132	3.5	253	14.3
52	13.4	86	3.2	134	3.6	254	59.2
53	10.1	87	3.4	154	6.0	255	14.0
61	7.9	91	12.9	155	72.6		
62	7.1	92	15.5	156	18.7		
63	3.2	93	4.1	157	72.6		

Peaks having intensities lower than 3% of the base peak and lower than m/e 15 are not reported.

Significant Ions in Support of Structure and Composition

m/e		m/e	
252	M^+	104	$C_6H_4CO^+$
183	$[M - CF_3]^+$	76	$C_6H_4^+$
155	$C_6H_4Br^+$		

combined. After stirring, the Freon solution was separated and washed with ice water (1 x 100 mL), saturated sodium bicarbonate solution (3 x 100 mL), and water (3 x 100 mL), then dried over anhydrous $MgSO_4$. Removal of solvent gave 87.7 g (89.0% yield) of crude product (GC purity 97%). Purification by distillation resulted in 79.2 g (80.4% yield) of clear colorless $C_2F_5C_6H_4Br$ (GC purity 99.9%), BP 96-97°C/86 mm Hg. The infrared and mass spectra are presented in Figure 9 and Table 8, respectively. When the SF_4 fluorination was carried out at ~200°C over extended period of time (~50 h) poor yield (34%) of $C_2F_5C_6H_4Br$ resulted and the production of sulfur containing by-products was observed. The latter were identified by their mass spectra given in Tables 9 and 10.

Preparation of p-$C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)C_6H_4Br$

Under nitrogen bypass, into a 2 L 3-neck round bottom flask containing 1,4-dibromobenzene (59 g, 0.25 mol) and freshly distilled ether (500 mL) at -15°C was added n-butyllithium (100 mL, 2.5M in hexanes, 0.25 mol) over a period of 1 h. After stirring for an additional 0.5 h at -15°C, the solution was cooled to -78°C and $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CO_2CH_3$ (128 g, 0.25 mol) dissolved in ether (50 mL) was added over 1.5 h. This was followed by stirring at -78°C for 1 h. Subsequently, hydrochloric acid (2N, 300 mL) was added and the solution allowed to stir at room temperature overnight. The organic layer was separated, and washed with water (3 x 100 mL), and dried over anhydrous $MgSO_4$.

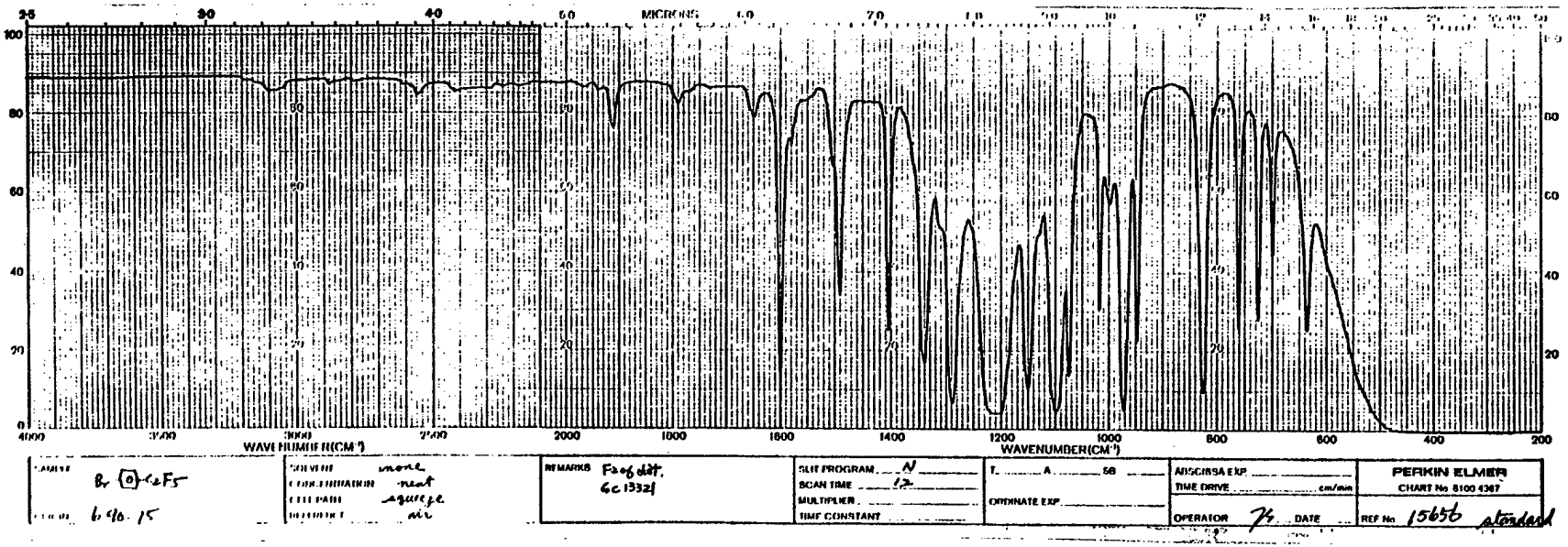


Figure 9. Infrared spectrum of $BrC_6H_4C_2F_5$.

TABLE 8

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF

$C_2F_5C_6H_4Br$ (MW 274)

m/e	%	m/e	%	m/e	%	m/e	%
26	3.2	76	24.2	104	5.1	155	12.6
27	3.3	77	8.7	105	8.3	156	5.2
31	12.2	78	4.2	106	7.8	157	9.1
37	8.3	79	10.8	107	19.9	195	3.2
38	11.5	80	15.3	108	3.0	196	4.2
39	7.9	81	18.0	117	3.3	205	96.9
49	7.3	82	9.7	119	7.4	206	25.2
50	32.9	85	6.0	123	4.9	207	100.0
51	17.3	86	5.7	124	9.8	208	24.7
56	4.7	87	8.0	125	42.2	223	8.3
57	10.8	88	5.8	126	71.2	225	8.3
61	7.9	93	3.5	127	20.5	255	18.7
62	12.1	94	3.3	128	4.2	256	3.2
63	16.4	95	10.6	137	3.5	257	18.2
68	4.0	99	17.3	143	5.5	258	3.1
69	22.2	100	14.2	144	16.4	274	80.6M^+
73	8.4	101	3.0	145	31.8	275	19.2
74	21.4	102	6.3	146	6.2	276	80.7
75	39.2	103	8.4	153	4.4	277	19.6

Peaks having intensities lower than 3% of the base peak and lower than m/e 15 are not reported.

Significant Ions in Support of Structure and Composition

m/e		m/e	
274	M^+	145	$CF_3C_6H_4^+$
255	$[M - F]^+$	126	$C_6H_4CF_2^+$
205	$[M - CF_3]^+$	76	$C_6H_4^+$
155	$C_6H_4Br^+$		

TABLE 9

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF

$[p\text{-}C_2F_5C_6H_3Br]_2S$

m/e	%	m/e	%	m/e	%	m/e	%
20	3.9	143	3.9	233	5.7	363	8.4
31	4.7	144	8.7	236	4.1	369	4.5
45	6.7	156	3.9	237	7.7	380	10.1
50	10.0	157	39.4	238	5.2	381	3.1
51	4.3	158	9.7	250	3.6	382	10.7
62	5.5	159	5.1	255	3.5	401	4.1
63	12.4	160	3.3	262	7.2	420	27.8
69	24.5	162	3.2	263	3.9	421	10.2
74	10.1	175	3.3	280	4.1	422	4.2
75	21.8	180	6.8	281	11.8	429	15.6
79	8.1	181	7.6	282	25.7	430	5.3
80	12.9	182	4.0	283	8.6	431	15.4
81	13.0	186	3.0	284	3.6	432	5.0
82	15.7	187	3.0	300	5.0	498	14.9
87	3.5	188	8.4	301	9.0	499	4.9
93	4.6	192	3.3	304	7.4	500	15.3
94	3.5	194	3.9	306	3.3	501	4.5
99	5.6	204	4.7	307	5.6	509	11.6
105	4.7	205	3.7	311	21.7	511	18.0
106	7.6	206	6.7	312	7.5	512	5.3
107	6.1	207	4.9	313	23.0	513	11.2
113	5.7	213	4.2	314	5.9	559	5.5
116	6.8	220	15.0	331	3.7	561	9.0
119	10.0	221	19.5	350	3.2	563	5.5
123	3.2	222	20.4	351	59.5	578	52.2
125	25.6	223	5.9	352	20.9	580	100.0
126	4.3	225	5.9	353	8.3	581	28.2
131	4.2	226	10.5	360	7.4	582	49.0
137	3.3	231	12.3	361	8.2	583	17.2
141	10.2	232	21.1	362	8.3	584	7.4

Peaks having intensities lower than 3% of the base peak and lower than m/e 20 are not reported.

Significant Ions in Support of Structure and Composition

m/e		m/e	
578	M^+	282	$[CF_2C_6H_3SC_6H_3CF_2]^+$
509	$[M - CF_3]^+$	231	$[C_6H_2SC_6H_3CF_2]^+$
498	$[M - HBr]^+$	226	$[CF_3CF_2C_6H_3S]^+$
429	$[M - HBr-CF_3]^+$	157	$[CF_2C_6H_3S]^+$
420	$[M - 2Br]^+$	125	$[CF_2C_6H_3]^+$
351	$[CF_2C_6H_3SC_6H_3C_2F_5]^+$		

TABLE 10

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF

$[p\text{-}C_2F_5C_6H_3Br]_2S_2$

m/e	%	m/e	%	m/e	%	m/e	%
17	4.4	112	3.2	227	6.1	429	40.5
18	23.1	113	6.8	231	12.2	430	7.9
20	8.3	119	5.4	232	3.1	431	38.8
28	32.6	123	4.3	235	7.0	432	8.0
31	5.1	124	3.3	236	6.9	433	3.2
32	8.4	125	15.6	237	14.0	441	4.7
38	3.4	131	3.4	238	6.4	452	18.9
44	4.1	137	3.0	239	4.7	453	4.1
45	11.4	140	5.4	258	3.3	460	4.5
50	9.3	143	7.3	260	4.9	491	6.7
51	4.9	144	4.3	261	5.3	493	4.0
57	3.0	155	4.6	280	3.7	498	21.7
61	3.5	156	6.4	281	11.5	499	4.6
62	8.7	157	100.0	282	3.7	500	23.3
63	20.8	158	14.7	300	3.0	501	4.8
69	43.8	159	8.2	305	21.4	507	3.2
73	7.7	175	3.8	306	7.9	508	5.4
74	14.7	180	6.8	307	20.5	509	7.6
75	22.7	181	6.8	308	6.2	510	11.2
79	9.9	186	3.5	310	3.2	511	5.4
80	18.5	189	4.6	312	3.3	512	5.8
81	17.0	192	3.7	349	4.4	578	6.2
82	22.8	194	3.4	350	3.8	580	6.0
85	3.0	203	3.3	351	6.3	610	27.0
87	3.3	205	4.7	360	9.4	611	6.0
93	5.3	207	10.8	362	7.8	612	48.6
99	4.8	220	6.4	383	8.5	613	12.2
105	6.1	222	3.4	389	5.1	614	30.1
106	12.6	225	3.7	391	8.4	615	5.9
107	7.6	226	44.6	393	5.6	616	3.6

Peaks having intensities lower than 3% of the base peak and lower than m/e 20 are not reported.

Significant Ions in Support of Structure and Composition

m/e		m/e	
610	M^+	305	$[CF_3CF_2C_6H_3(S)Br]^+$
498	$[M - HBr - S]^+$	226	$[CF_3CF_2C_6H_3S]^+$
452	$[M - 2Br]^+$	157	$[CF_2C_6H_3S]^+$
429	$[M - HBr - S - CF_3]^+$	125	$[CF_2C_6H_3]^+$

The crude product (145 g) was heated in vacuum, <50°C, to remove volatile liquid and solid byproducts. Distillation of the residue (131 g) gave 119 g (75% yield) of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)C_6H_4Br$, BP 60-65°C/0.001 mm Hg (GC purity >99%).

Preparation of $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4Br$

Into a Parr bomb (125 mL) containing Freon-113 (25 mL) and $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)C_6H_4Br$ (60 g, 94.8 mmol), cooled with Dry Ice, was added (under nitrogen flow) anhydrous hydrogen fluoride (~10 mL). The bomb was closed off and maintained at -78°C. Subsequently, sulfur tetrafluoride (25 g, 0.23 mol) was condensed in. After warming to room temperature, the bomb was agitated, using a shaker assembly, at 100-110°C (sand bath) for 20 h. Following cooling to room temperature and venting, Freon-113 (50 mL) was added and the reaction mixture was poured onto ice-water (100 mL). The reactor was rinsed with additional Freon-113 (50 mL) and the combined solution was washed with a saturated sodium bicarbonate solution (4 x 50 mL), water (3 x 50 mL), and dried over anhydrous $MgSO_4$. Solvent removal resulted in 60 g of viscous product containing a fluffy solid, which was removed by filtration. This was followed by distillation to give 58.7 g (94.2% yield) of $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4Br$, BP 50-51°C/0.001 mm Hg (GC purity >99.5%).

Attempted preparation of $(C_6H_5O)_2P(O)C_6H_4C_2F_5$

Under nitrogen bypass to a stirred mixture of tetrahydrofuran (20 mL), magnesium turnings (0.5 g, 19 mmol), $C_2F_5C_6H_4Br$ (0.5 g) and a crystal of iodine in a bath kept at 60°C was added $C_2F_5C_6H_4Br$ (4.5 g, 16.4 mmol) at such a rate as to maintain a gentle reflux. After completion of addition, the reaction mixture was refluxed for 1 h. Subsequently, the Grignard (cooled to room temperature) was added to a stirred solution of $ClP(O)(OC_6H_5)_2$ (5.9 g, 1.8 mmol) in tetrahydrofuran (20 mL)at 0°C over 0.5 h. Stirring at 0°C was continued for another 0.5 h. After warming to room temperature, 2N hydrochloric acid (50 mL) was added slowly and followed by diethyl ether (100 mL). The organic layer, after washing, drying over anhydrous $MgSO_4$ and solvent evaporation gave 7.8 g of liquid found by GC/MS to consist of $C_6H_5OP(O)(C_6H_4C_2F_5)_2$ plus $(C_2F_5C_6H_4)_3P(O)$ 19%, $(C_6H_5O)_2P(O)C_6H_4C_2F_5$ 50%, and $(C_6H_5O)_3P(O)$ 26%. The mass spectrum of $(C_6H_5O)_2P(O)C_6H_4C_2F_5$ is presented in Table 11.

Preparation of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4C(CH_3)_2OH$

A 250 mL three-neck round bottom flask equipped with nitrogen bypass inlet, magnetic stirring bar, and two addition funnels was charged with $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4Br$ (10.0 g, 15.2 mmol), followed by anhydrous diethyl ether (20 mL). To one of the addition funnels was added, via a double tip needle, n-butyllithium (8 mL, 2.5M solution in hexanes) and to the other freshly distilled acetone (2.0 g, 34 mmol). n-Butyllithium

TABLE 11

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF

$(C_6H_5O)_2P(O)C_6H_4C_2F_5$ (MW 428)

m/e	%	m/e	%	m/e	%	m/e	%
18	9.1	74	3.7	145	10.3	272	3.4
20	15.9	75	8.5	152	4.0	288	44.9
26	3.9	76	10.5	155	3.2	289	10.8
27	4.6	77	100.0	157	3.1	317	5.0
28	26.7	78	24.6	168	6.7	333	17.4
31	3.4	93	6.4	169	13.0	334	7.6
32	4.8	94	46.7	170	31.3	335	32.4
38	7.0	95	7.7	171	6.9	336	8.1
39	29.6	96	4.2	173	4.4	351	5.6
40	4.9	107	3.6	176	3.7	359	4.0
47	19.1	115	3.0	183	12.4	409	10.9
50	17.6	119	3.0	185	9.9	426	11.7
51	40.6	125	5.2	189	9.1	427	86.8
52	4.1	126	12.5	199	3.1	428	81.1
55	3.4	127	8.1	201	3.6	429	31.3
63	9.8	139	8.0	203	4.5	430	5.9
64	6.1	140	12.8	217	10.7	443	5.1
65	31.5	141	9.0	219	15.5	444	9.3
66	13.7	142	3.6	259	3.9		
69	4.8	143	3.6	265	4.9		

Peaks having intensities lower than 3% of the base peak and lower than m/e 15 are not reported.

Significant Ions in Support of Structure and Composition

m/e		m/e	
428	$[M]^+$	145	$[C_6H_4CF_3]^+$
409	$[M - F]^+$	140	$[P(O)OC_6H_5]^+$
335	$[M - OC_6H_5]^+$	126	$[C_6H_4CF_2]^+$
288	$[C_6H_5OC_6H_4C_2F_5]^+$	94	$[C_6H_5OH]^+$
170	$[C_6H_5OC_6H_5]^+$	77	$[C_6H_5]^+$

solution was added at -7°C over 0.5 h to the bromide; the reaction mixture was subsequently stirred for 1 h. Following acetone addition the reaction mixture was stirred for an additional 1 h and then quenched with hydrochloric acid (25 mL, 2N). After additional diethyl ether (20 mL) was added, the organic layer was separated, washed with water (15 mL), and dried over anhydrous magnesium sulfate. Distillation under reduced pressure gave 7.0 g (72% yield) of the desired product. The mass spectrum is presented in Table 12; the infrared spectrum in Figure 10.

Attempted preparation of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4OH$ by acid promoted hydroperoxide rearrangement

To stirred hydrogen peroxide (1.0 g, 30% solution, 8.8 mmol) was added sulfuric acid (2.2 g, 95% solution) at 0°C over a period of 5 minutes. After stirring at 0°C for 0.5 h $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4C(CH_3)_2OH$ (2.0 g, 3.1 mmol) was added over a period of 5 minutes, and the reaction mixture was stirred for 2 h at 0°C, then for 18 h at room temperature. Following pouring into of water (25 mL) and extraction with diethyl ether (50 mL), the organic layer was washed with water (25 mL), saturated sodium bicarbonate solution (25 mL) and dried over anhydrous magnesium sulfate. Solvent removal (under reduced pressure) gave 1.9 g of product found to consist of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C_6H_4OH$ (identified as the silylated derivative) and $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C_6H_4C(O)CH_3$ in an

TABLE 12

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF

$C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4C(CH_3)_2OH$

m/e	%	m/e	%	m/e	%	m/e	%
15	8.3	95	5.0	153	16.9	227	7.7
18	10.8	97	11.4	154	17.6	235	6.4
20	5.8	99	5.9	155	6.9	239	6.0
28	5.7	100	20.6	156	6.3	241	9.6
29	7.8	101	10.2	157	8.1	245	5.1
31	24.9	102	7.8	158	6.7	247	6.2
39	13.1	103	5.5	163	5.3	248	5.5
41	32.1	105	6.7	164	15.7	249	7.4
42	9.0	107	9.3	165	22.0	251	9.4
43	59.7	109	5.2	166	12.1	267	30.1
44	18.1	114	7.2	167	86.2	268	13.8
45	6.2	115	20.2	168	35.5	269	12.4
47	14.9	116	20.5	169	54.4	270	8.9
50	20.5	117	12.0	170	32.2	271	7.1
51	13.6	119	25.4	171	13.5	273	6.4
53	5.8	120	8.3	172	5.7	333	11.0
55	5.2	123	6.1	173	6.0	335	11.0
57	10.2	125	13.4	176	8.9	383	6.2
58	8.0	126	23.4	177	7.3	431	5.2
59	56.7	127	40.0	178	5.6	433	12.8
60	9.2	128	13.1	182	5.3	436	6.2
62	5.9	131	12.1	183	10.0	499	6.5
63	8.8	133	12.5	184	7.8	517	13.5
65	13.0	134	5.8	185	28.4	599	14.8
66	7.3	135	7.3	186	9.9	600	6.0
69	59.0	137	7.3	187	9.8	605	27.7
70	6.6	138	7.0	191	7.3	606	9.2
74	6.5	139	6.7	195	11.7	616	27.6
75	12.5	140	19.5	198	11.2	618	38.8
76	8.8	141	22.8	199	5.1	619	50.1
77	16.2	142	5.3	201	15.8	620	30.2
78	11.1	143	6.4	203	5.5	621	100.0
81	8.1	145	21.1	207	7.3	622	37.3
82	5.5	146	17.9	215	7.8	623	15.6
85	21.9	147	19.5	217	19.7	624	5.3
88	5.1	148	5.0	218	5.7	635	10.1
89	6.9	150	15.6	219	6.8		
91	14.9	151	22.9	220	12.8		
92	6.5	152	16.3	221	6.2		

Peaks having intensities lower than 5% of the base peak and lower than m/e 15 are not reported.

Significant Ions in Support of Structure and Composition

m/e		m/e		m/e	
59	$C(CH_3)_2OH^+$	185	$CF_2C_6H_4C(CH_3)OH^+$	621	$[M - CH_3]^+$
167	$CF_2C_6H_4CHO^+$	335	$C_3F_7OCF(CF_3)CF_2^+$	635	$[M - H]^+$

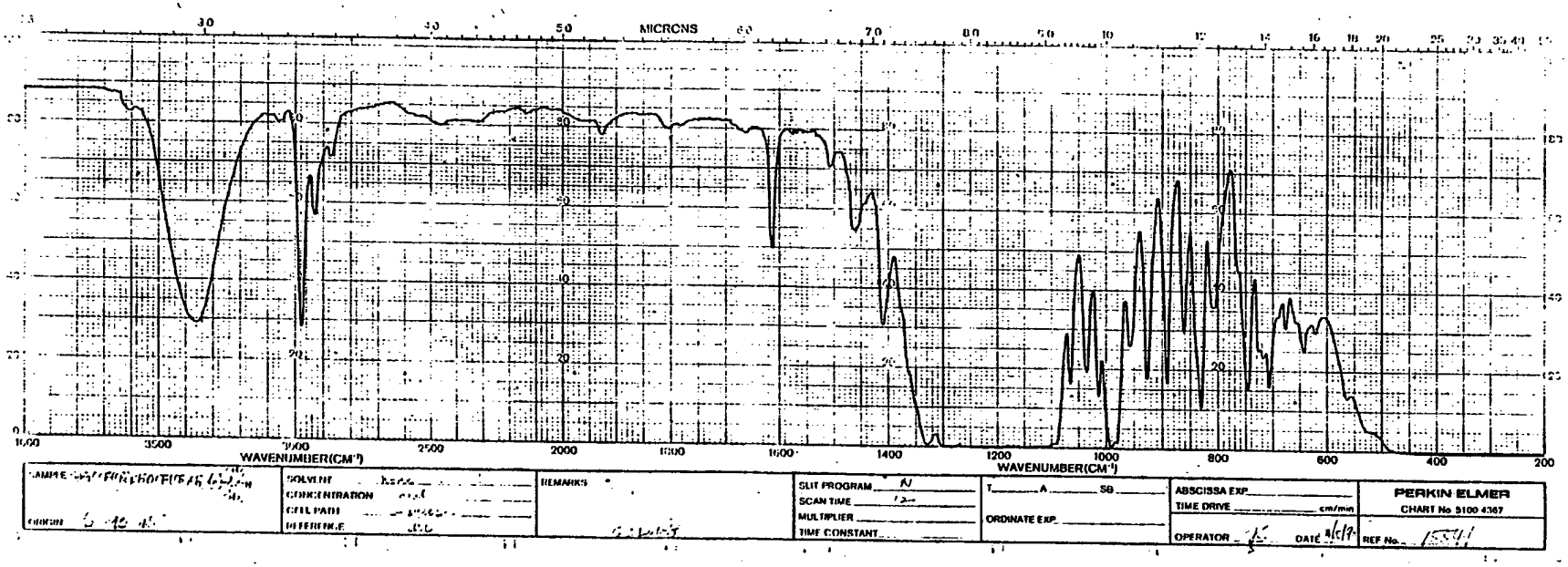


Figure 10. Infrared spectrum of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4C(CH_3)_2OH$.

approximate ratio of 1:2; the respective MS data are given in Tables 13 and 14.

Preparation of 2-chloro-1,3,2-dioxaborolane

Into a 250 mL three-neck round bottom flask cooled in Dry Ice-acetone bath (equipped with magnetic stirring bar, two Dry Ice condensers, and nitrogen bypass inlet) was added through the Dry Ice condenser boron trichloride (29.6 g, 252 mmol). This was followed by slow addition (1 h) of anhydrous ethylene glycol (14.9 g, 240 mmol). Subsequently, the cooling bath was removed, and the reaction mixture was allowed to warm to ambient temperature over a period of 1.5 h. The crude product was purified by distillation (BP 60-64°C/0.001 mm Hg) to give 13.60 g (53% yield) of 2-chloro-1,3,2-dioxaborolane.

Preparation of 2-t-butylperoxy-1,3,2-dioxaborolane

Under nitrogen bypass, to a stirred solution of 2-chloro-1,3,2-dioxaborolane (12.6 g, 118 mmol), in benzene (50 mL) was added over 20 minutes tert-butyl hydroperoxide (40 mL, 3.0 M solution in 2,2,4-trimethylpentane, 120 mmol) admixed with pyridine (9.35 g, 118.2 mmol). This was followed, after 10 minutes, by diethyl ether (50 mL), to complete the precipitation of pyridine hydrochloride. Stirring was continued for 3 h and the precipitate filtered off. The solvents were then removed in vacuo

TABLE 13

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4OSiMe_3$ (MW 666)

m/e	%	m/e	%	m/e	%	m/e	%
15	5.5	77	58.1	149	4.2	269	19.1
20	5.7	78	10.5	150	10.2	270	3.5
28	23.4	79	8.2	164	4.6	281	16.4
29	4.6	81	7.7	169	26.0	282	3.2
31	7.5	85	8.8	185	3.3	283	5.6
32	5.8	86	7.7	193	3.2	296	17.4
36	3.3	91	8.3	195	3.4	297	4.4
43	12.8	93	7.3	199	7.4	299	47.2
44	6.7	100	42.9	200	3.3	300	19.5
45	29.1	101	3.9	207	6.5	301	9.9
47	12.9	107	4.3	211	4.2	315	20.5
49	5.6	115	4.9	213	5.0	316	17.4
50	6.2	119	11.9	215	100.0	317	7.3
51	3.1	125	4.2	216	37.1	319	6.0
58	3.7	126	6.5	217	17.4	381	4.2
59	5.3	127	8.9	219	24.3	415	7.7
63	8.4	131	4.7	220	4.7	465	3.7
69	44.8	133	7.0	223	8.5	485	7.4
72	4.1	135	5.3	231	3.1	547	3.1
73	91.6	137	3.0	233	3.4	647	5.3
74	20.0	140	4.4	239	3.1	651	4.7
75	19.6	145	4.4	247	3.7	666	28.4
76	4.8	147	5.7	265	7.3	667	8.2

Peaks having intensities lower than 3% of the base peak and lower than m/e 15 are not reported.

Significant Ions in Support of Structure and Composition

m/e		m/e	
666	M^+	169	$C_3F_7^+$
647	$[M - F]^+$	77	$C_6H_5^+$
315	$CF(CF_3)CF_2C_6H_4OSiMe_3^+$	73	$SiMe_3^+$
215	$CF_2C_6H_4OSiMe_3^+$		

TABLE 14

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4C(O)CH_3$ (MW 620)

m/e	%	m/e	%	m/e	%	m/e	%
14	6.4	99	6.7	158	5.2	242	5.8
15	12.7	100	20.1	159	4.7	245	6.4
20	5.6	101	7.8	167	7.5	249	17.7
28	13.2	104	2.3	168	4.4	250	6.8
31	13.8	105	3.9	169	69.5	251	14.0
38	3.2	106	4.1	170	20.4	252	3.1
39	5.6	107	12.5	171	9.5	253	6.4
42	9.6	108	3.1	172	5.6	254	9.6
43	53.5	114	4.9	173	19.4	255	8.0
44	10.2	119	20.3	174	5.9	269	40.2
47	13.8	120	5.8	175	4.3	270	13.2
50	20.1	123	4.1	176	15.6	271	3.3
51	11.2	124	3.9	177	6.3	273	6.4
57	4.6	125	19.2	181	4.2	319	3.0
62	6.7	126	46.7	182	6.1	335	16.6
63	8.2	127	37.8	185	17.7	336	5.1
64	3.0	128	9.0	186	4.3	367	8.6
65	4.6	131	11.0	187	7.7	401	3.6
66	8.6	137	6.7	191	10.0	417	6.7
69	50.0	138	8.4	195	18.9	435	18.1
70	6.0	139	6.0	196	5.1	436	6.2
74	7.5	140	21.2	199	4.6	501	7.6
75	14.7	141	23.2	200	5.2	551	8.0
76	13.9	142	6.3	201	10.5	578	5.3
77	17.9	143	4.5	204	9.9	592	38.2
78	7.5	144	4.9	205	4.6	601	25.9
81	8.7	145	24.8	207	7.2	602	9.1
85	3.4	146	6.8	219	12.1	605	100.0
87	4.6	147	8.0	220	3.1	606	45.8
88	4.6	150	16.2	221	5.6	607	16.9
89	5.5	151	8.1	222	3.9	608	4.7
90	4.0	152	3.6	223	3.4	620	35.7
91	9.0	153	5.1	225	12.8	621	18.5
93	3.9	154	43.8	226	8.4	622	5.5
95	5.7	155	16.0	227	9.3		
96	3.2	156	7.3	235	9.1		
97	11.5	157	10.8	241	17.8		

Peaks having intensities lower than 3% of the base peak and lower than m/e 14 are not reported.

Significant Ions in Support of Structure and Composition

m/e		m/e		m/e	
620	M^+	269	$CF(CF_3)CF_2C_6H_4C(O)CH_3^+$	126	$CF_2C_6H_4^+$
605	$[M - CH_3]^+$	169	$CF_2C_6H_4C(O)CH_3^+$	43	$C(O)CH_3^+$
592	$[M - CO]^+$	154	$CF_2C_6H_4CO^+$		

to give 9.9 g of material assumed to consist of 2-t-butylperoxy-1,3,2-dioxaborolane.

Reaction of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4Li$ with 2-t-butylperoxy-1,3,2-dioxaborolane

To $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4Br$ (7.8 g, 11.9 mmol), in diethyl ether (20 mL) at -7°C was added n-butyllithium (5.0 mL, 2.5 M solution in hexanes, 12.5 mmol) over a period of 15 minutes; stirring at -7°C was continued for 3 h. Subsequently, via a double-tip needle, the reaction mixture was added at -7°C to 2-t-butylperoxy-1,3,2-dioxaborolane (1.6 g, 13.1 mmol) in diethyl ether (20 mL) over a period of 5 minutes. The reaction mixture was then stirred at room temperature for 20 h, followed by heating at a gentle reflux for 3 h. After cooling and the addition of diethyl ether (50 mL) and aqueous HCl (50 mL, 1.2 N), the organic layer was separated, washed with water (50 mL), dried over anhydrous magnesium sulfate and evaporated to give 6.6 g of residue. Based on GC/MS it consisted of mainly $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4OH$ ~17% (MS, Table 15) and $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_5$ ~67% (MS, Table 16).

Preparation of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)C_6H_4OCH_3$

Into a 300 mL three-neck round bottom flask equipped with magnetic stirring bar, nitrogen bypass inlet, two addition funnels, and rubber septum was introduced p-bromoanisole (4.46 g, 23.8 mmol), followed by diethyl ether (50 mL). To one of the

TABLE 15

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF

$C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4OH$ (MW 594)

m/e	%	m/e	%	m/e	%	m/e	%
43	7.2	121	2.4	169	17.6	223	10.5
45	2.6	142	4.1	170	2.0	224	2.2
63	2.6	143	100.0	171	2.7	243	15.2
65	2.2	144	16.2	173	2.3	309	2.3
69	12.3	145	10.1	174	4.0	409	2.4
95	4.8	150	2.1	183	5.5	574	3.3
100	4.7	151	2.3	192	2.0	575	2.3
114	7.3	153	2.4	193	13.0	594	$7.7M^+$
119	10.3	155	2.4	214	6.2		

Peaks having intensities lower than 2% of the base peak and lower than m/e 15 are not reported.

Significant Ions in Support of Structure and Composition

m/e		m/e	
594	M^+	169	$C_3F_7^+$
574	$[M - HF]^+$	143	$CF_2C_6H_4OH^+$
243	$CF(CF_3)CF_2C_6H_4OH^+$		

TABLE 16

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF

$C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_5$ (MW 578)

m/e	%	m/e	%	m/e	%	m/e	%
20	4.8	76	6.5	129	5.5	190	3.0
27	4.3	77	30.4	131	7.3	195	4.6
28	17.8	78	10.5	138	4.6	204	3.1
31	16.9	79	4.9	145	10.6	205	3.4
39	6.9	81	8.0	146	7.1	207	20.3
47	12.1	88	3.6	147	4.9	208	8.4
50	23.9	96	7.3	150	10.7	224	4.9
51	21.3	97	7.0	155	6.1	227	48.3
52	4.0	99	4.1	157	4.4	228	13.4
57	4.8	100	18.4	158	13.2	323	5.3
62	4.3	101	7.8	169	26.1	373	4.5
63	6.5	107	9.7	170	3.1	393	11.0
66	5.7	108	6.9	176	3.5	509	3.4
69	54.2	119	19.0	177	24.9	559	7.6
70	4.6	125	7.9	178	5.6	578	24.2M^+
73	3.0	126	16.7	187	3.4	579	8.7
74	5.2	127	100.0	188	3.5		
75	10.4	128	47.8	189	3.1		

Peaks having intensities lower than 3% of the base peak and lower than m/e 20 are not reported.

Significant Ions in Support of Structure and Composition

m/e		m/e	
578	M^+	177	$CF_2CF_2C_6H_5^+$
393	$[M - C_3F_7O]^+$	127	$CF_2C_6H_5^+$
227	$CF(CF_3)CF_2C_6H_5^+$	77	$C_6H_5^+$

addition funnels was added n-butyllithium (11 mL, 2.5 M solution in hexanes, 27.5 mmol) and to the other was added $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CO_2CH_3$ (11.0 g, 21.6 mmol). n-Butyllithium was added to p-anisole at -45°C over 20 minutes. The temperature was then raised to ~-5°C and stirring was continued for 3 h. The progress of the reaction was monitored by GC. Subsequently, the reaction mixture was cooled again to -45°C and the methyl ester added over a 20 minute period. Stirring was continued for an additional 2 h. The reaction mixture was quenched with dilute hydrochloric acid (1 N, 100 mL). Following the addition of diethyl ether (25 mL) the organic layer was separated, washed with water (2 x 50 mL), and dried over anhydrous magnesium sulfate. After solvent removal, 11.5 g of a dark brown liquid was obtained which based on GC/MS analysis consisted of $p\text{-}BrC_6H_4OCH_3$ (3%), $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)C_6H_4OCH_3$ (Table 17, 43%), and $1\text{-}C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)\text{-}2\text{-}OCH_3\text{-}5\text{-}Br\text{-}C_6H_3$ (Table 18, 19%).

Fluorination of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)C_6H_4OCH_3$ with SF_4

A 125 mL stainless steel Parr pressure reactor was charged with $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)C_6H_4OCH_3$ (4.0 g, 6.8 mmol), followed by Freon-113 (6 mL). Under N_2 atmosphere, the reactor was briefly cooled in a Dry Ice-acetone bath and anhydrous hydrogen fluoride (2 mL) was poured in. After the addition, the reactor was closed immediately and placed again in a Dry Ice-acetone bath. Sulfur tetrafluoride (11 g, 98 mmol) premeasured in a storage cylinder was transferred into the reactor

TABLE 17

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF

$C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)C_6H_4OCH_3$ (MW 586)

m/e	%	m/e	%	m/e	%	m/e	%
15	5.8	65	3.8	100	12.9	154	3.8
20	4.4	66	5.8	104	8.2	157	11.7
28	7.2	69	39.0	105	3.9	169	20.9
31	12.5	74	3.7	106	3.3	207	20.4
38	6.3	75	5.9	107	21.4	208	3.7
39	5.6	76	10.6	108	4.7	235	4.6
47	8.5	77	29.1	119	11.6	301	5.8
50	14.6	78	9.2	120	5.9	373	3.4
51	7.9	79	6.3	131	3.8	401	9.6
53	4.8	81	3.1	135	100.0	467	4.4
62	4.2	92	25.2	136	28.2	567	8.7
63	14.1	93	5.7	137	8.6	586	14.6M^+
64	21.2	97	4.1	150	7.3	587	4.7

Peaks having intensities lower than 3% of the base peak and lower than m/e 15 are not reported.

Significant Ions in Support of Structure and Composition

m/e		m/e	
586	M^+	135	$CH_3OC_6H_4CO^+$
207	$CH_3OC_6H_4CF(CF_3)^+$	107	$CH_3OC_6H_4^+$
169	$C_3F_7^+$	92	$OC_6H_4^+$

TABLE 18

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF

$C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)C_6H_3Br(OMe)$ (MW 664)

m/e	%	m/e	%	m/e	%	m/e	%
15	8.9	82	7.8	169	27.9	217	6.1
20	6.1	90	3.1	170	24.7	229	4.1
28	16.9	91	5.9	171	5.2	231	6.3
29	7.1	94	3.6	172	22.7	232	3.2
31	14.5	97	9.1	173	5.3	233	4.1
37	3.9	100	18.7	175	4.6	234	5.6
38	3.8	105	4.6	181	3.4	235	3.9
39	5.6	106	11.9	182	3.6	237	4.4
47	9.9	107	6.8	183	5.1	285	8.2
50	20.1	118	4.8	184	4.3	287	6.5
51	12.2	119	21.6	185	7.2	313	8.4
53	6.1	131	7.2	186	3.3	314	3.8
61	4.6	133	3.2	187	5.8	315	8.8
62	11.7	134	20.5	189	3.9	335	4.2
63	29.0	135	14.0	198	13.9	379	3.4
64	5.5	142	8.1	199	5.0	380	4.3
66	5.0	144	8.2	200	13.0	381	3.7
69	66.4	147	7.0	201	5.5	645	4.3
74	10.2	150	10.1	203	4.1	647	4.2
75	22.9	153	7.3	204	3.1	664	24.5M^+
76	22.0	154	7.0	205	6.4	665	7.8
77	14.1	155	23.1	207	5.4	666	23.2
78	22.5	156	8.5	213	98.9	667	7.7
79	8.3	157	22.9	214	24.8		
80	7.2	158	16.3	215	100.0		
81	9.3	159	4.9	216	23.8		

Peaks having intensities lower than 3% of the base peak and lower than m/e 15 are not reported.

Significant Ions in Support of Structure and Composition

m/e		m/e	
664	M^+	170	$BrC_6H_3O^+$
585	$[M - Br]^+$ (1.4%)	155	$BrC_6H_4^+$
213	$BrC_6H_3(OCH_3)CO^+$	134	$CH_3OC_6H_3CO^+$

which was then heated in a sand bath at ~200°C for 37 h while agitated with a mechanical shaker. Subsequently, the reactor was placed in an ice-water bath, vented, and the contents poured onto crushed ice and water. The organic layer was separated, washed with aqueous sodium bicarbonate and water, and dried over magnesium sulfate. The solvent was removed under reduced pressure to give 4.60 g of a gummy yellow residue. GC analysis of this material in Freon-113 failed to show any peaks at the retention times expected for the product; no peaks corresponding to the starting material were observed.

Optimized Preparation of $C_2F_5C_6H_4OH$

Under nitrogen bypass, into a 500 mL 3-neck round bottom flask containing freshly distilled ether (150 mL) and n-butyllithium (46 mL, 2.5 M in hexanes, 115.0 mmol), was added $C_2F_5C_6H_4Br$ (21.0 g, 76.4 mmol) dissolved in ether (30 mL) at -10°C over a period of 0.5 h. The resultant reaction mixture, after stirring at -10°C for additional 1.5 h (the reaction was found to be complete after 0.5 h by GC analysis), was added (without warming) over a period of 50 minutes (via a double-tip needle) to another 500 mL 3-neck round bottom flask (cooled to -10°C) containing trimethyl borate (36.0 g, 346 mmol) and ether (75 mL). Stirring at -10°C was continued for additional 2 h. Subsequently, acetic acid (21.0 g, 333 mmol) was added and the resultant solution stirred for 0.75 h. This was followed by the addition (at -10°C) of hydrogen peroxide (30%, 35 mL, 343 mmol, in H_2O 35

mL). The reaction mixture was allowed to warm to room temperature and stirred overnight. Water (325 mL) and ether (200 mL) were added. The organic layer was separated, combined with the ether (100 mL) extract of the aqueous layer, and washed with ferrous sulfate solution (25 g $FeSO_4.7H_2O$, 10 mL concentrated hydrochloric acid, 25 mL H_2O), water, and, then dried over anhydrous $MgSO_4$. Solvent removal followed by sublimation at 50°C afforded 11.7 g (72.2% yield) of $C_2F_5C_6H_4OH$, MP 95-98°C. The infrared spectrum of the alcohol and the mass breakdown pattern of the trimethylsilyl derivative are presented in Figure 11 and Table 19, respectively. Preparations carried out are summarized in Table 20.

Preparation of $(C_2F_5C_6H_4O)P(O)(OC_6H_5)_2$ (I)

In an inert atmosphere enclosure to $C_2F_5C_6H_4OH$ (2.50 g, 11.8 mmol) in benzene (7 mL) was introduced $P(O)Cl(OC_6H_5)_2$ (3.16 g, 11.8 mmol) in benzene (13 mL), followed by addition of triethylamine (2.41 g, 23.8 mmol) in benzene (8 mL), added over a 15 minute period. The resultant reaction mixture was stirred at room temperature for 0.5 h, then heated under nitrogen bypass for 20 h at 85°C. The precipitated $Et_3N \cdot HCl$ was filtered off; the solvent was removed from the filtrate to give 4.7 g (90% yield) of a light yellow liquid (GC purity 98%). Purification by distillation gave 3.9 g (75% yield) of clear, colorless $(C_2F_5C_6H_4O)P(O)(OC_6H_5)_2$, BP 144-146°C/0.001 mm Hg, (GC purity >98%). The infrared spectrum is given in Figure 12; the mass spectrum in Table 21 and the TGA in Figure 13.

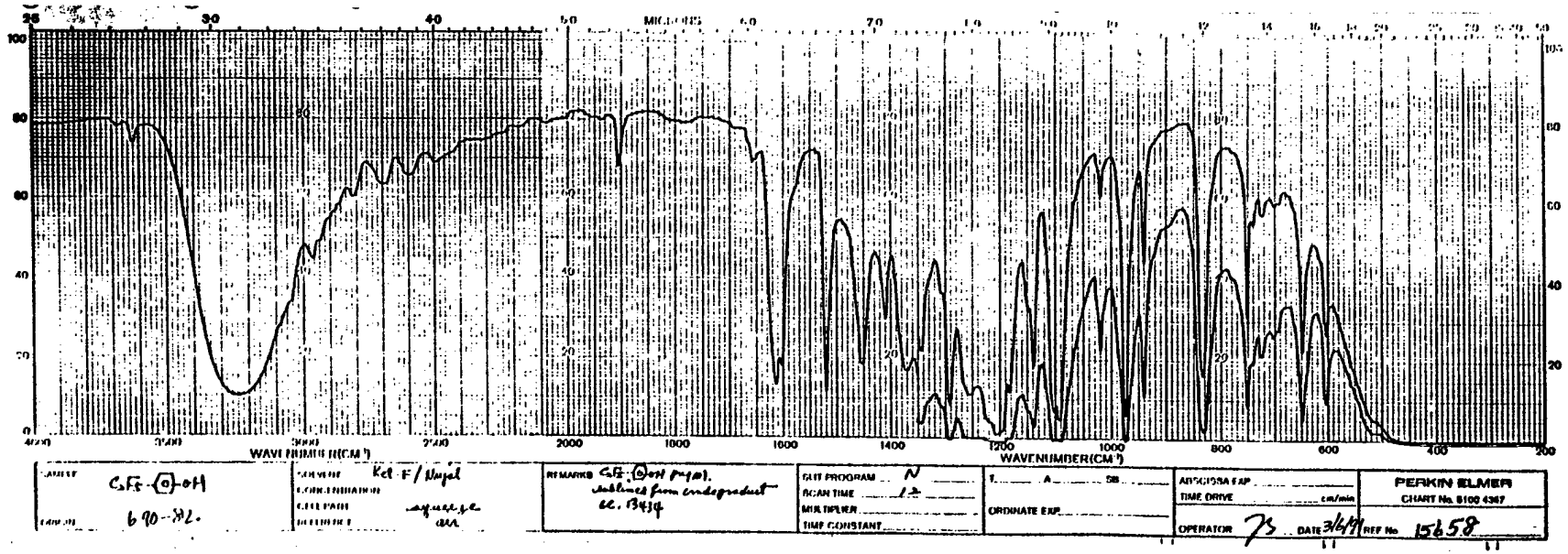


Figure 11. Infrared spectrum of $C_2F_5C_6H_4OH$.

TABLE 19

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF

$C_2F_5C_6H_4OSi(CH_3)_3$ (MW 284)

m/e	%	m/e	%	m/e	%	m/e	%
15	5.3	73	30.7	121	3.9	220	4.1
27	3.0	74	8.3	125	7.8	239	8.9
28	7.6	75	17.9	126	6.1	253	5.8
29	7.2	76	4.7	127	6.5	255	15.3
31	3.5	77	27.7	135	9.7	265	12.4
43	16.0	78	3.8	140	5.8	266	4.0
44	8.0	79	6.1	143	3.6	267	3.7
45	22.6	81	7.3	145	14.3	269	100.0
47	8.8	85	6.3	149	7.6	270	40.7
49	5.1	86	9.0	150	8.9	271	21.8
50	5.6	87	3.3	151	3.3	272	3.5
51	3.9	91	5.7	195	3.7	284	68.6
57	3.8	93	3.4	199	9.3	285	28.9
58	3.7	95	4.6	209	3.8	286	12.1
59	4.8	100	16.8	215	18.8	288	3.0
63	7.4	101	8.1	216	5.3		
69	5.1	114	5.3	219	17.2		

Peaks having intensities lower than 3% of the base peak and lower than m/e 15 are not reported.

Significant Ions in Support of Structure and Composition

m/e		m/e	
284	$[M]^+$	145	$[CF_3C_6H_4]^+$
269	$[M - CH_3]^+$	77	$[C_6H_5]^+$
265	$[M - F]^+$	73	$[Si(CH_3)_3]^+$
215	$[M - CF_3]^+$		

TABLE 20

SUMMARY OF PREPARATIONS OF $C_2F_5C_6H_4OH$

	STEP 1						STEP 2				STEP 3						
											HOAc Soln		H_2O_2 Soln				
Rxn No.	$C_2F_5C_6H_4Br$ g	mmol	n-BuLi mL	mmol	Et_2O mL	Time[a] min	$B(OMe)_3$ g	mmol	Et_2O mL	Time[a] min	HOAc g	H_2O mL	H_2O_2[b] mL	H_2O mL	Time[c] hr	$C_2F_5C_6H_4OH$[d] g	yield%
1[e]	5	18.2	8	20.0	50	100	2.29	22.0	10	180	1.8	16	8	10	1.5	1.2	31
2	10	36.4	16	40.0	100	95	4.57	44.0	50	75	3.6	32	16	20	2.0	4.3	56
3	10	36.4	16	40.0	100	105	4.72	45.4	50	85	3.6	32	16	20	15.5	1.3	17
4[e]	10	36.4	17	42.5	125	120	4.85	46.7	50	75	3.6	32	16	20	1.0	0.4	5
5	5	18.2	10	25.0	50	140	2.55	24.5	25	90	1.9	0	8	10	1.0	0.8	20
6	5	18.2	9	22.5	50	120[f]	2.61	25.1	25	120[f]	1.8	0	16	20	15.0	1.6	41
7	10	36.4	18	45.0	100[g]	75[f]	5.41	52.1	50	80[f]	3.6	0	32	40	15.5	2.8	36
8	10	36.4	20	50.0	100[h]	90[f]	5.83	56.1	50	120[i]	3.6	0	32	40	15.5	2.3	30
9	10	36.4	18	45.0	100[h]	100[j]	5.20	50.0	50	110[j]	3.8	0	32	40	21.5	2.3	30
10	21	76.4	46	115	180[k]	90[f]	36.0	346	75	120[f]	21	0	35	35	15.5	11.7	72

a) Stirred for the denoted period after addition of the reagent at -6°C unless otherwise noted.
b) Hydrogen peroxide 30 wt. % solution in water.
c) Stirred at room temperature for the denoted period after addition of the reagents at -6°C. Reagents were added at -10°C for reaction No. 6, 7 and 10; at -15°C for reaction No. 9.
d) $C_2F_5C_6H_4OH$ purified by sublimation.
e) In this reaction the n-BuLi was added to the reaction flask containing the $C_2F_5C_6H_4Br$ and ether.
f) This step conducted at -10°C.
g) 50 ml ether was added to the bromide.
h) 25 ml ether was added to the bromide.
i) Temperature was raised to -6°C after 1 hr at -10°C.
j) This step conducted at -15°C.
k) 30 ml ether was added to the bromide.

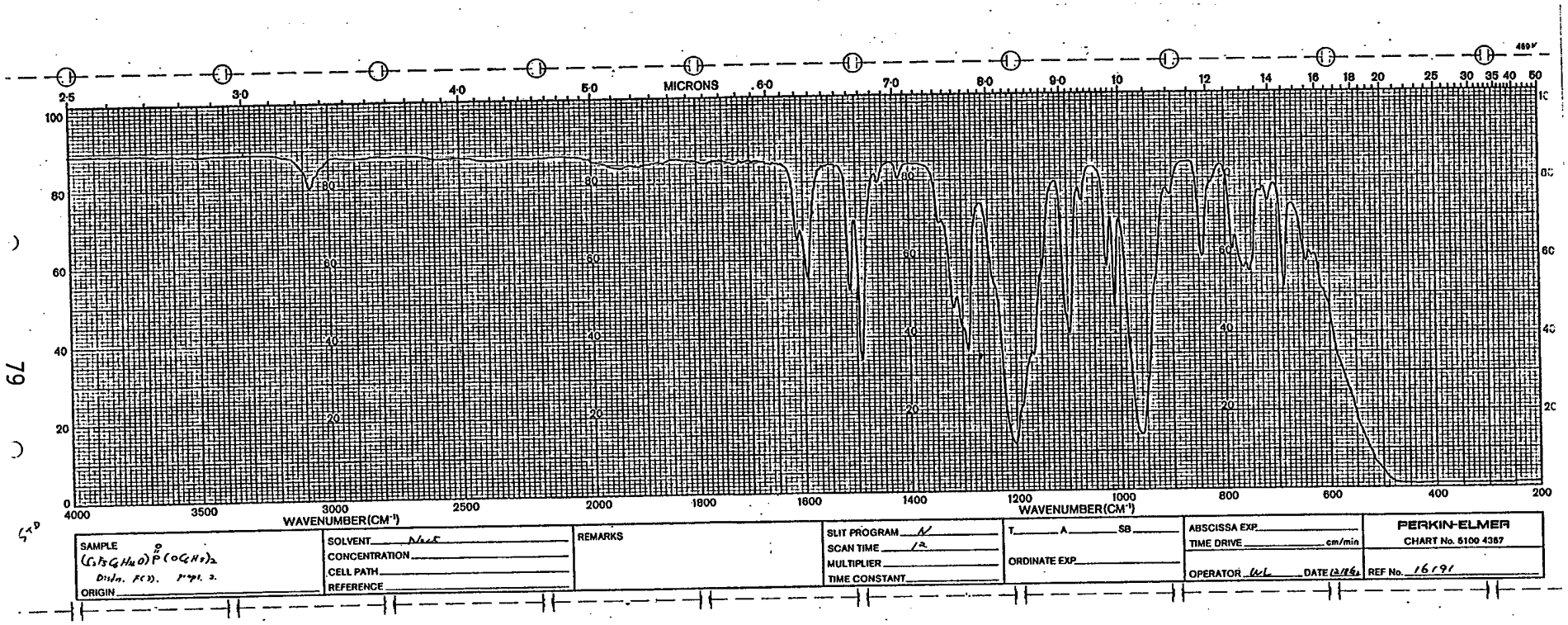


Figure 12. Infrared spectrum of $C_2F_5C_6H_4OP(O)(OC_6H_5)_2$ (I).

TABLE 21

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF

$C_2F_5C_6H_4OP(O)(OC_6H_5)_2$ (MW 444)

m/e	%	m/e	%	m/e	%	m/e	%
39	15.2	93	11.9	169	14.7	277	13.1
47	9.1	94	48.8	170	16.7	281	5.5
50	5.8	95	5.5	187	24.7	288	9.4
51	20.6	139	10.8	189	5.7	333	6.2
63	8.4	140	14.2	205	15.0	351	6.2
64	3.9	141	7.0	215	24.7	375	8.8
65	34.9	142	3.9	216	3.4	425	3.8
66	3.8	143	12.5	217	7.5	443	56.2
75	4.7	145	11.0	219	23.2	444	74.8M
76	4.8	152	6.4	220	3.5		
77	100.0	156	4.1	232	8.7		
78	6.7	168	14.3	233	9.4		

Peaks having intensities lower than 3% of the base peak are not reported.

Significant Ions in Support of Structure and Composition

m/e

444 - M^+

443 - $[M - H]^+$

425 - $[M - F]^+$

375 - $[M - CF_3]^+$

351 - $[M - OC_6H_5]^+$

233 - $[M - OC_6H_4C_2F_5]^+$

232 - $[M - OC_6H_4C_2F_5 - H]^+$

143 - $[CF_2C_6H_4OH]^+$

140 - $[OPOC_6H_5]^+$

94 - $[C_6H_5OH]^+$

77 - $[C_6H_5]^+$

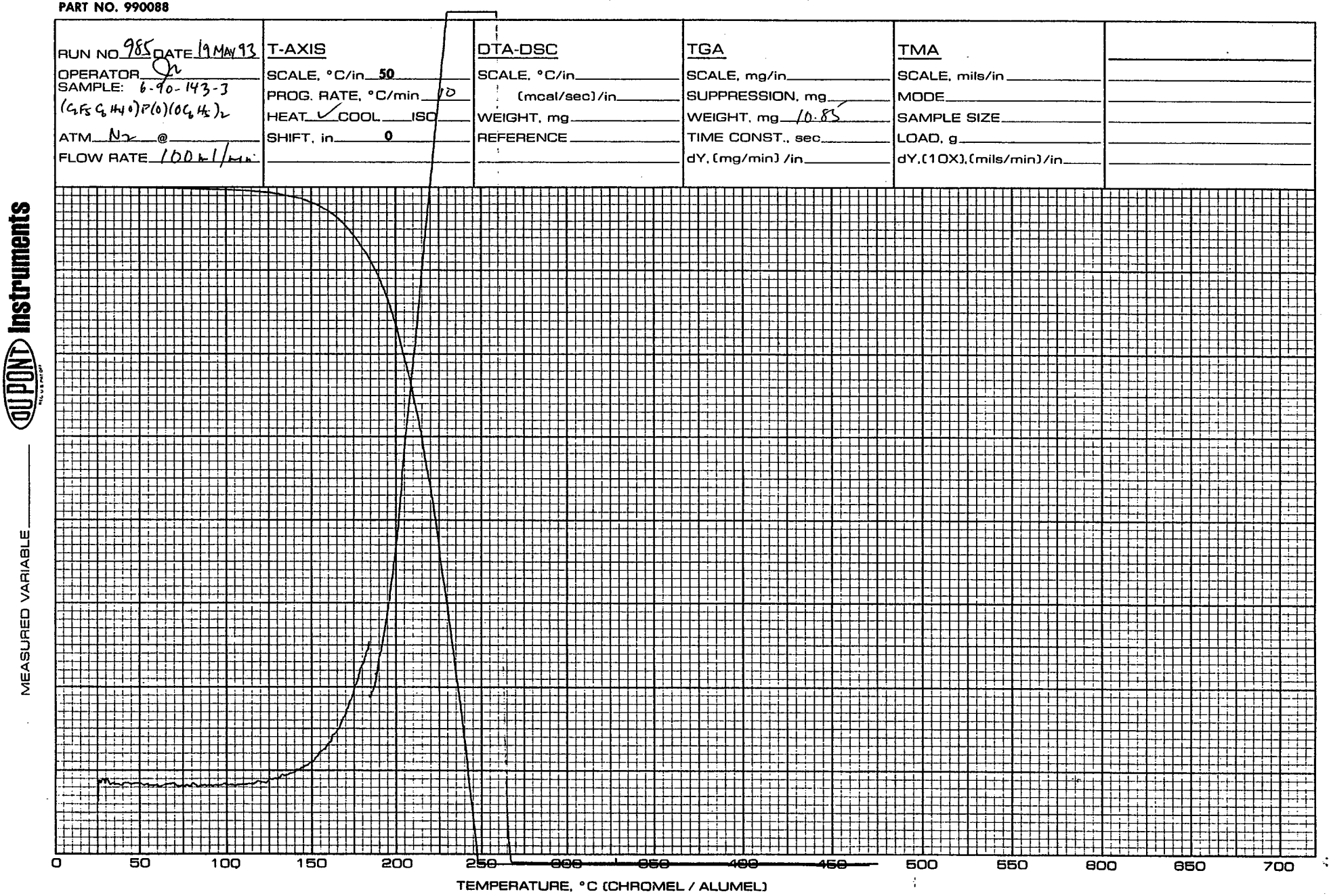


Figure 13. TGA of $C_2F_5C_6H_4OP(O)(OC_6H_5)_2$ (I) in N_2.

Preparation of $(C_2F_5C_6H_4O)P(O)(C_6H_5)_2$ (II)

In an inert atmosphere enclosure to $C_2F_5C_6H_4OH$ (2.50 g, 11.8 mmol) in benzene (19 mL) was introduced over 5 minutes $(C_6H_5)_2P(O)Cl$ (2.79 g, 11.8 mmol) in benzene (10 mL), followed by the addition of triethylamine (2.39 g, 23.6 mmol) in benzene (5 mL) over a period of 15 minutes. A white cloud appeared immediately; this was followed by precipitation of fine white solid. After stirring at room temperature in the inert atmosphere enclosure for 0.5 h, the reaction mixture was heated at 85°C under nitrogen bypass for 19 h. Following cooling to room temperature, the solid ($Et_3N \cdot HCl$) was filtered off. From the filtrate solvent was removed in vacuo to give 4.7 g (97% yield) of light yellow solid, (GC purity 95%). Recrystallization from hexanes (30 mL) afforded 4.2 g (86% yield) of white solid $(C_2F_5C_6H_4O)P(O)(C_6H_5)_2$, MP 69-71°C (GC purity 97%). The infrared spectrum is given in Figure 14; the mass spectrum in Table 22 and the TGA in Figure 15.

Preparation of $(C_2F_5C_6H_4O)_2P(O)OC_6H_5$ (III)

In an inert atmosphere enclosure, into a stirred solution of $C_2F_5C_6H_4OH$ (3.00 g, 14.1 mmol) and $C_6H_5OP(O)Cl_2$ (1.49 g, 7.06 mmol) in benzene (7 mL) was added (via an addition funnel) over a period of 0.5 h a solution of triethylamine (2.9 g, 28.3 mmol) in benzene (8 mL). After stirring for additional 0.5 h at room temperature, the reaction mixture was heated at 85°C for 20 h under nitrogen bypass. After cooling, the precipitated

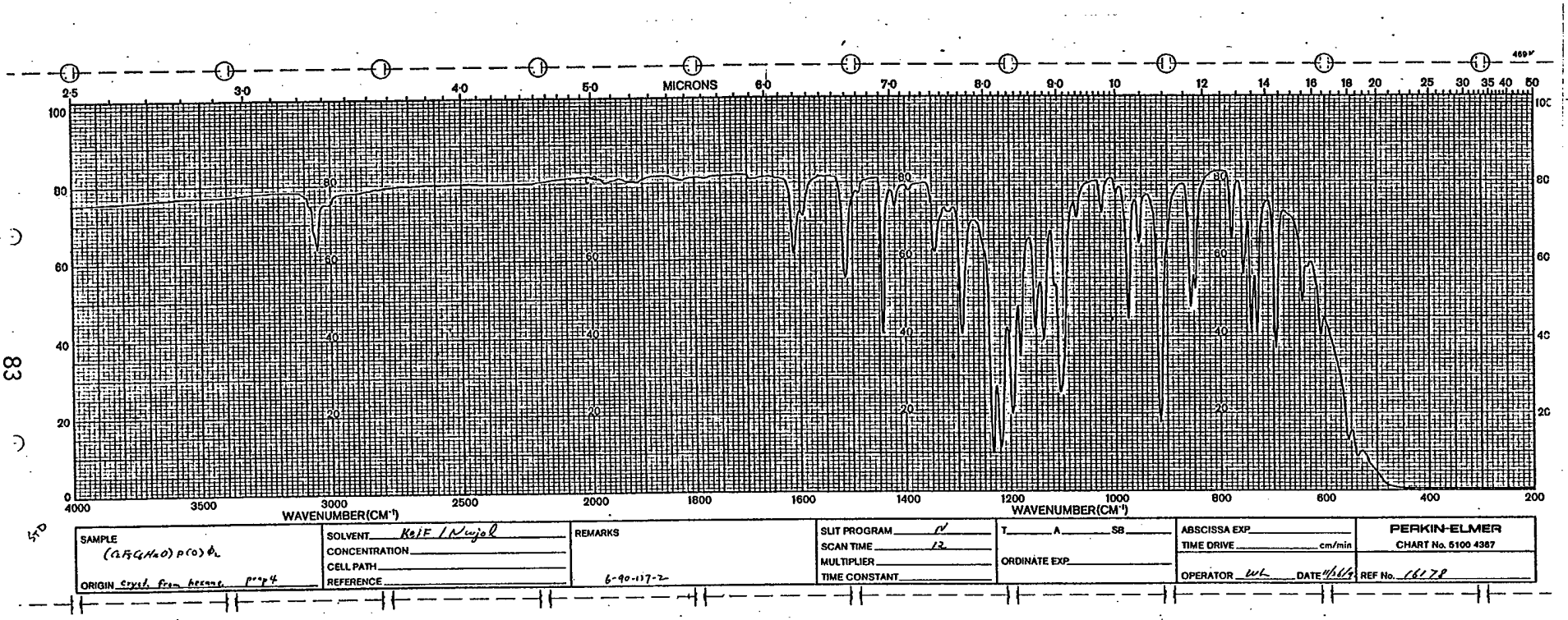


Figure 14. Infrared spectrum of $C_2F_5C_6H_4OP(O)(C_6H_5)_2$ (II).

TABLE 22

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF

$C_2F_5C_6H_4OP(O)(C_6H_5)_2$ (MW 412)

m/e	%	m/e	%	m/e	%	m/e	%
18	6.5	88	5.0	145	10.5	202	36.5
20	3.7	95	15.6	151	3.5	203	5.0
27	4.8	107	5.6	152	14.1	217	4.4
39	7.7	114	17.8	153	11.2	219	6.2
47	25.9	115	4.8	154	14.1	288	4.6
50	14.0	123	6.8	163	5.3	335	3.2
51	43.9	125	5.6	170	3.8	343	4.6
52	5.1	126	3.1	171	13.7	393	5.3
63	7.6	128	7.1	172	4.0	410	7.3
69	8.0	129	5.6	173	11.0	411	67.1
75	6.1	133	5.9	183	14.3	412	63.4M
76	5.1	141	3.6	199	10.1	413	25.7
77	60.9	142	3.4	200	3.4	414	3.9
78	12.5	143	10.2	201	100.0		

Peaks having intensities lower than 3% of the base peak and lower than m/e 15 are not reported.

Significant Ions in Support of Structure and Composition

m/e

412 - M^+

393 - $[M - 19]^+$

201 - $[M - OC_6H_4C_2F_5]^+$

171 - $[C_2F_3C_6H_2O]^+$

143 - $[FPOC_6H_5]^+$

77 - $[C_6H_5]^+$

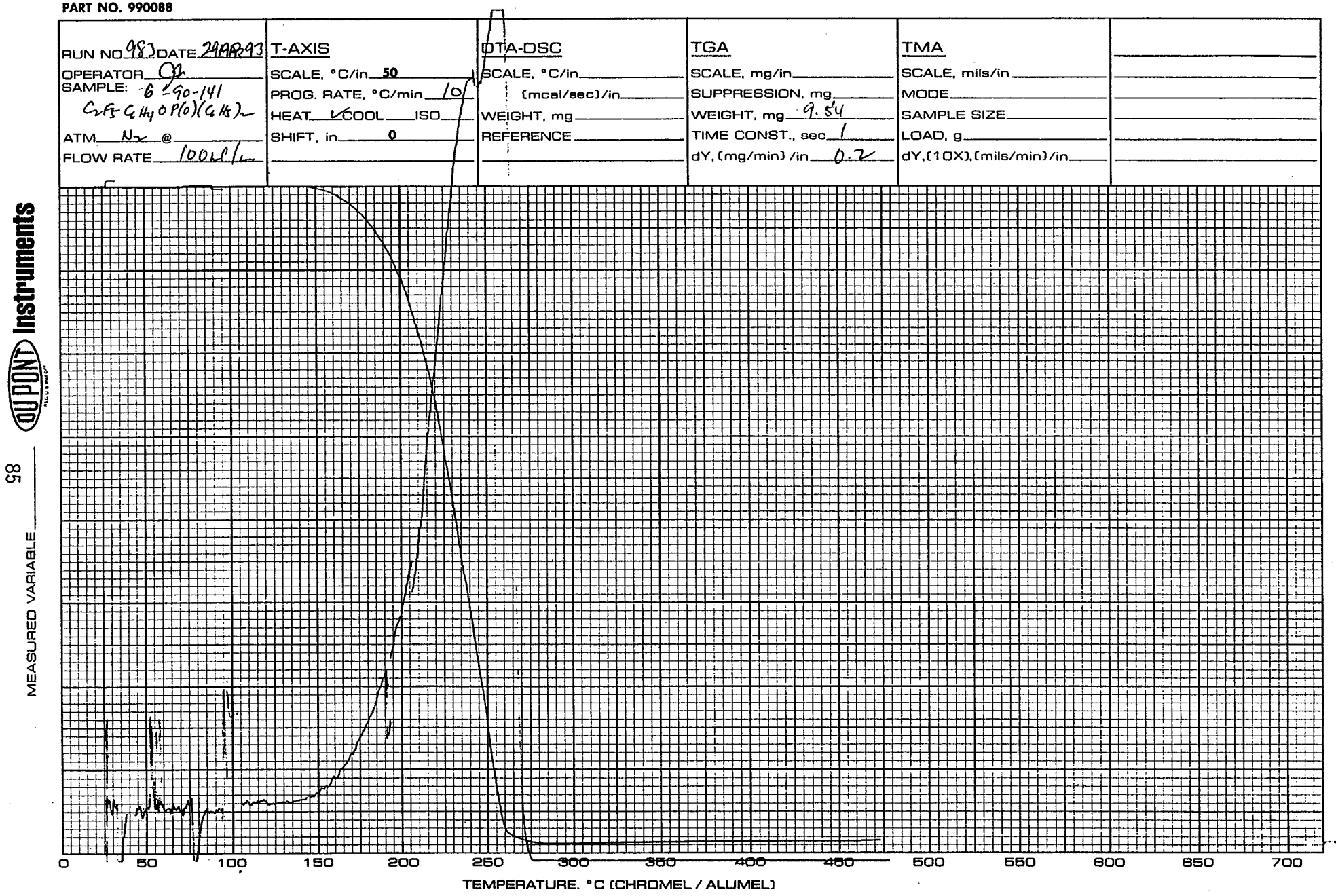


Figure 15. TGA of $C_2F_5C_6H_4OP(O)(C_6H_5)_2$ (II) in N_2.

triethylamine hydrochloride was filtered off. Solvent removal from the filtrate followed by pumping at 50°C gave 3.9 g of light brown liquid. After distillation, 3.0 g (75.6% yield) of $(C_2F_5C_6H_4O)_2P(O)(OC_6H_5)$, BP 144-146°C/0.001 mm Hg, (GC purity >99%) was obtained. Its infrared spectrum is given in Figure 16, its mass spectrum in Table 23 and the TGA in Figure 17.

Preparation of $(C_2F_5C_6H_4O)_3P(O)$ (IV)

In an inert atmosphere enclosure to a solution of $C_2F_5C_6H_4OH$ (1.20 g, 5.66 mmol), $POCl_3$ (0.29 g, 1.89 mmol) and benzene (5 mL) was added triethylamine (1.2 g, 11.4 mmol) in benzene (5 mL) over a period of 0.5 h. After an additional 0.5 h, the reaction mixture was heated at 85°C for 18 h under nitrogen bypass. The precipitated triethylamine hydrochloride was filtered off. The residue, following solvent removal from the filtrate, was dried <u>in vacuo</u> at 70°C to give 1.30 g (quantitative yield) of powdery solid, MP 87-89°C. Recrystallization from hexanes (8 mL) afforded 1.12 g (87% yield) of $(C_2F_5C_6H_4O)_3P(O)$, MP 89-90°C, (GC purity >99%). The infrared spectrum is given in Figure 18, the mass spectrum in Table 24 and the TGA scan in Figure 19.

Preparation of $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OH$

Under nitrogen bypass to n-butyllithium (40 mL, 2.5 M in hexanes, 100 mmol) and ether (225 mL) at -15°C was added $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4Br$ (52.69 g, 80.20 mmol), mixed with ether (15 mL), over a period of 1 h. After stirring for an additional

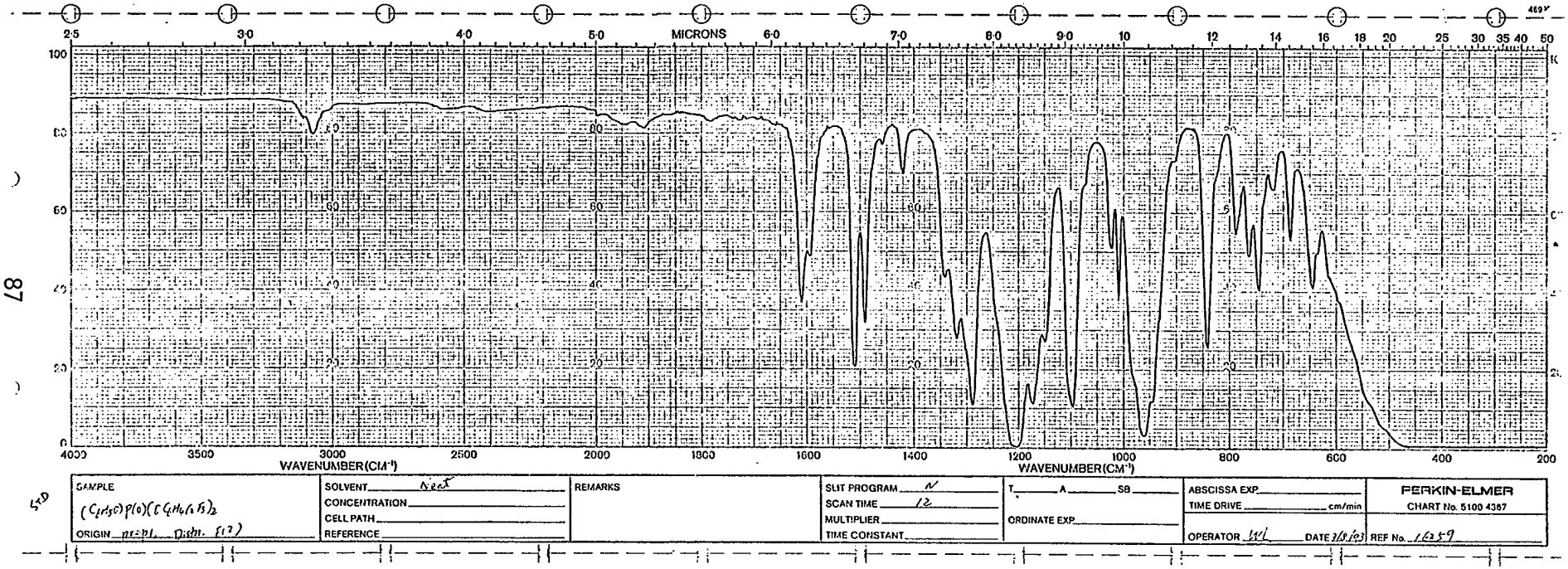


Figure 16. Infrared spectrum of $(C_2F_5C_6H_4O)_2P(O)OC_6H_5$ (III).

TABLE 23

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF

$(C_2F_5C_6H_4O)_2P(O)OC_6H_5$ (MW 562)

m/e	%	m/e	%	m/e	%	m/e	%
31	3.6	78	7.8	144	4.1	333	8.4
39	20.4	88	5.7	145	28.2	337	6.6
47	22.4	93	9.0	156	3.9	351	14.0
50	12.1	94	28.3	163	6.8	395	10.6
51	25.2	95	8.8	168	5.2	493	31.5
63	14.2	113	3.6	189	16.5	494	8.0
64	5.1	114	14.1	193	5.6	543	10.9
65	30.9	125	5.2	205	30.5	561	52.5
66	4.4	126	3.9	212	25.0	562	98.3M^+
69	7.4	127	4.6	217	6.7	563	24.5
75	9.9	139	3.6	219	21.0	564	4.7
76	4.1	140	14.9	281	8.1		
77	100.0	143	26.8	288	9.2		

Peaks having intensities lower than 3% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e

562 - M^+

543 - $[M - F]^+$

493 - $[M - CF_3]^+$

351 - $[M - C_2F_5C_6H_4O]^+$

212 - $C_2F_5C_6H_4OH^+$

143 - $CF_2C_6H_4OH^+$

77 - $C_6H_5^+$

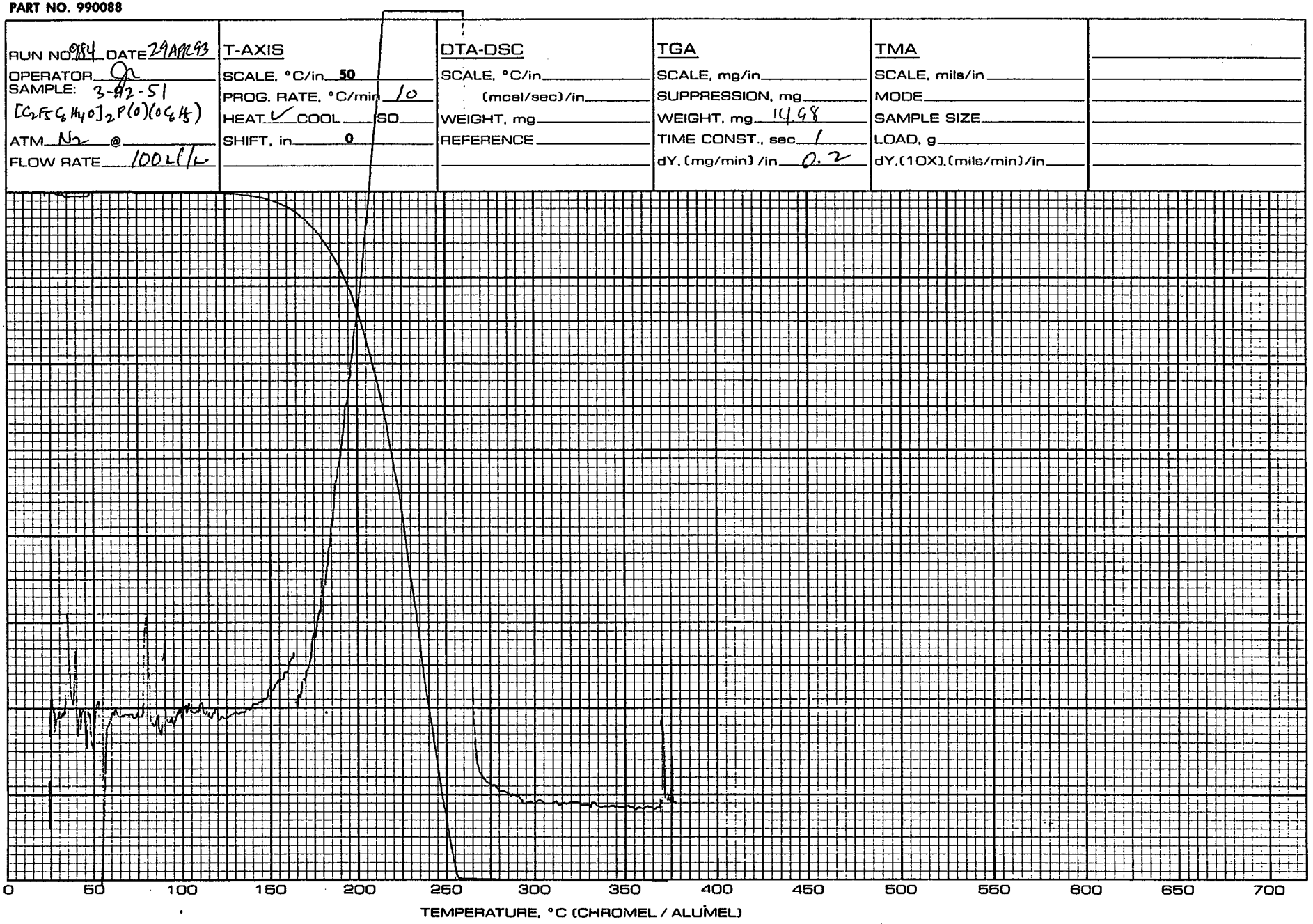


Figure 17. TGA of $(C_2F_5C_6H_4O)_2P(O)OC_6H_5$ (III) in N_2.

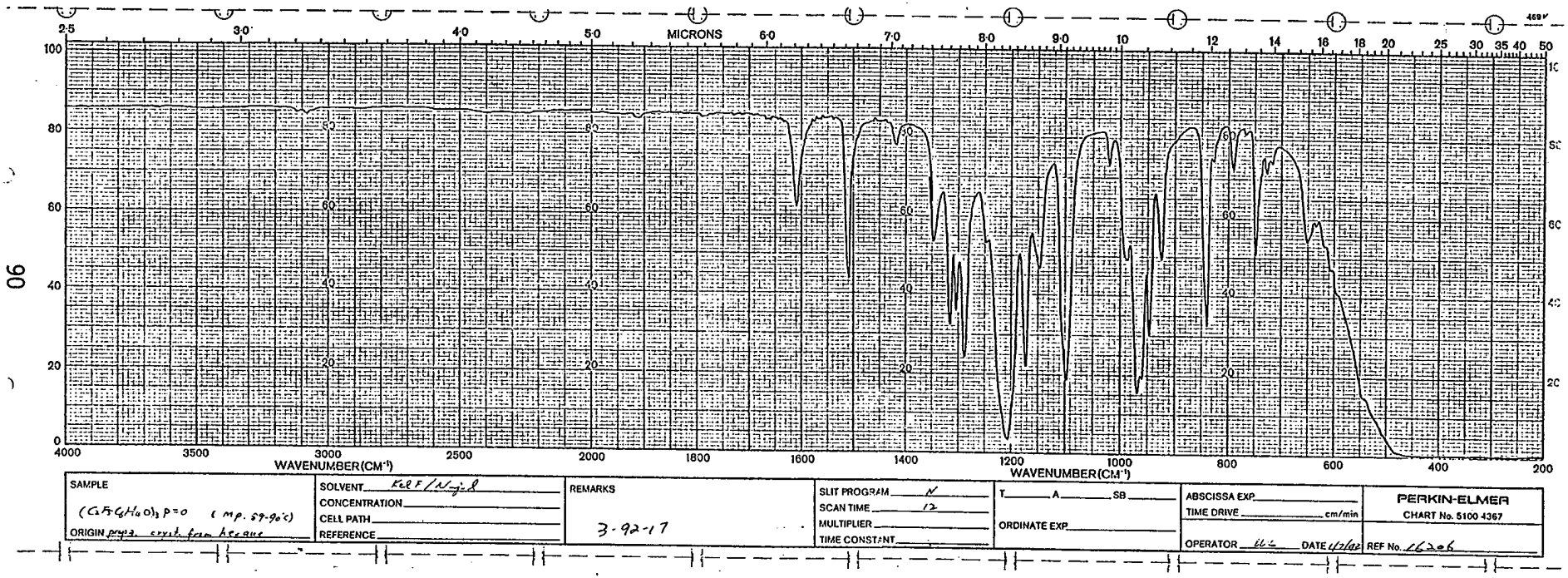


Figure 18. Infrared spectrum of $(C_2F_5C_6H_4O)_3P(O)$ (IV).

TABLE 24

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF

$(C_2F_5C_6H_4O)_3P(O)$ (MW 680)

m/e	%	m/e	%	m/e	%	m/e	%
47	8.0	146	7.8	217	3.8	406	5.5
69	7.6	158	6.5	239	4.8	450	18.5
75	6.1	163	16.0	246	34.0	469	16.4
88	3.7	183	4.5	257	6.4	470	3.0
95	6.0	189	51.5	271	74.2	485	5.1
113	5.0	190	5.8	296	9.1	513	16.6
114	20.8	193	15.1	309	4.5	514	4.1
125	10.3	195	12.5	335	11.1	530	3.4
126	8.2	205	39.1	337	35.5	563	3.4
133	4.4	206	3.9	338	5.3	611	77.9
141	3.0	207	3.5	399	20.0	612	20.7
143	33.3	211	3.6	400	3.8	613	3.8
145	100.0	212	5.3	401	6.4		

Peaks having intensities lower than 3% of the base peak are not reported.

Significant Ions in Support of Structure and Composition

m/e

611 - $[M - CF_3]^+$

469 - $[M - OC_6H_4C_2F_5]^+$

450 - $[M - OC_6H_4C_2F_5 - F]^+$

399 - $[M - OC_6H_4C_2F_5 - CF_3 - H]^+$

271 - $[C_2F_4C_6H_4OP(O)_3]^+$

189 - $[CF_2C_6H_4OPO]^+$

145 - $[CF_3C_6H_4]^+$

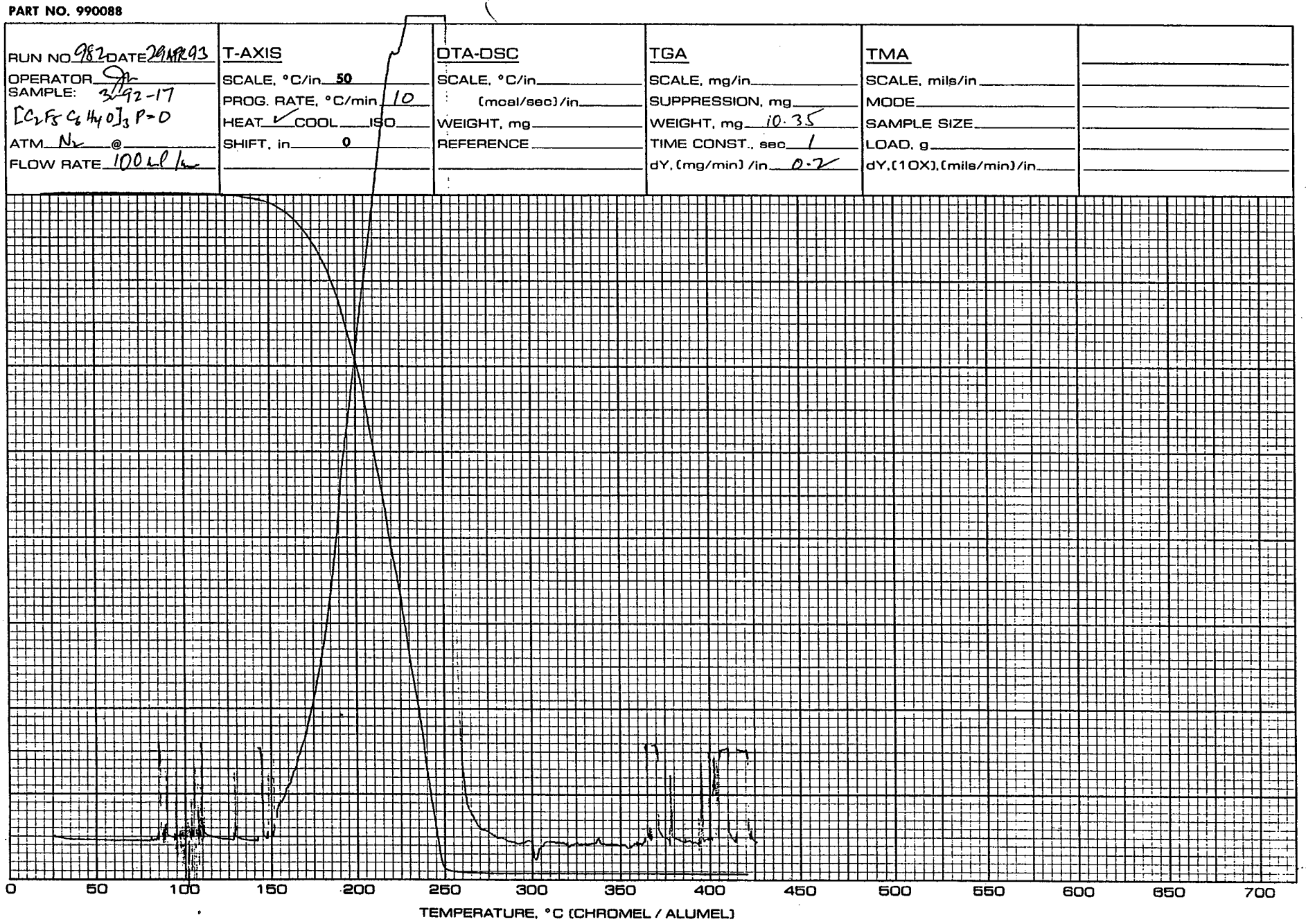


Figure 19. TGA of $(C_2F_5C_6H_4O)_3P(O)$ (IV) in N_2.

1 h at -15°C, the cold solution was added at -15°C over 1 h (via a double-tip needle) to a solution of trimethyl borate (36.6 g, 352 mmol; distilled over sodium) in ether (225 mL). After 2 h of stirring, acetic acid (21 g, 0.35 mol) was added and the solution was stirred for an additional 40 minutes. To the yellow solution, at -15°C, was then added hydrogen peroxide (30%, 52 mL, 0.5 mol) in H_2O (50 mL). Following stirring overnight at room temperature, water (250 mL) was added. The organic layer was washed with ferrous sulfate solution (20 g $FeSO_4.7H_2O$, 8 mL concentrated hydrochloric acid, 20 mL H_2O), water, and dried over anhydrous $MgSO_4$. After solvent removal, the product (46.0 g, 97% yield) was purified by passing through a silica gel column (150 g, 3.0 cm x 44 cm, packed in 5% ether/hexanes). Elution using 5% ether/hexanes (370 mL), resulted in the recovery of 4.79 g (from the first yellow band) of essentially pure $C_3F_7[OCF(CF_3)CF_2]_2C_6H_5$. The 20% ether/hexanes (50 mL) and 50% (430 mL) eluates gave 40 g of material (mainly in the 50% eluate; the second yellow band); which consisted of 92% (by GC) of $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OH$. This material was further purified by distillation to give 35.9 g (75% yield) of $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OH$, BP 63-65°C/0.001 mm Hg, (GC purity 99%). The infrared spectrum is presented in Figure 20. The preparations carried out are summarized in Table 25.

Preparation of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4OP(O)(OC_6H_5)_2$ (V)

In an inert atmosphere enclosure, into a stirred solution of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4OH$ (2.11 g, 3.55 mmol),

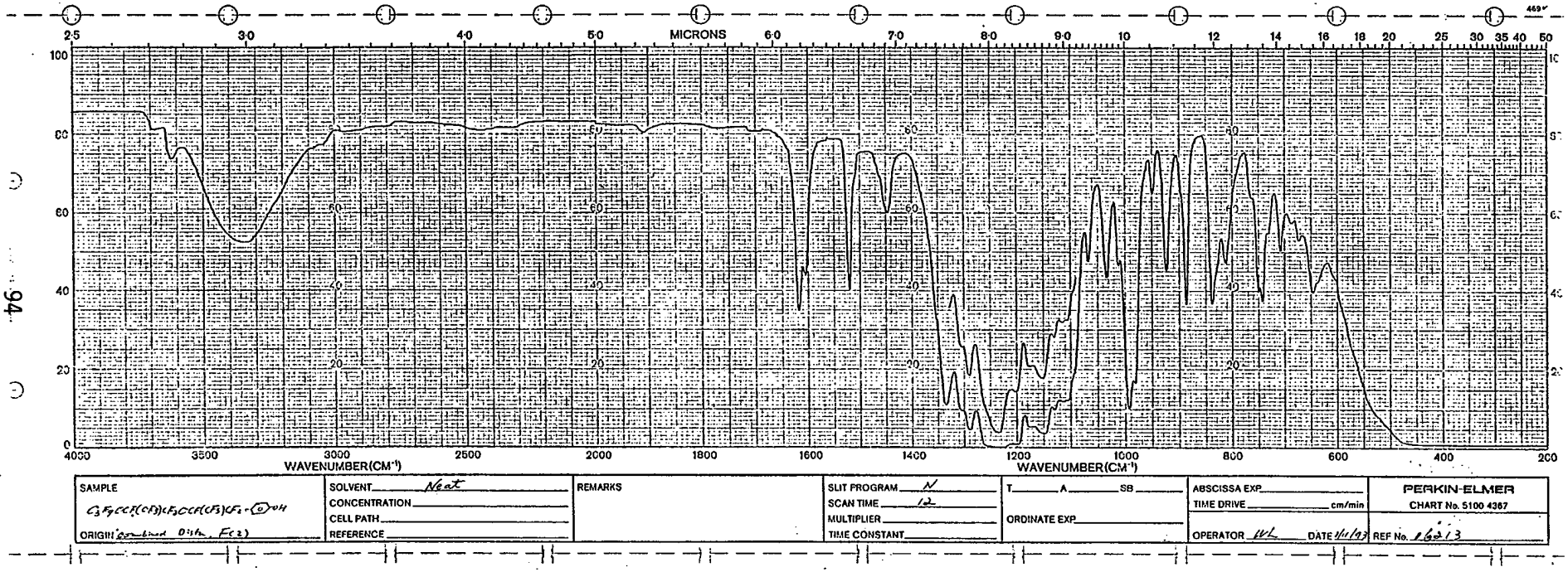


Figure 20. Infrared spectrum of $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OH$.

TABLE 25

SUMMARY OF PREPARATIONS OF $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OH$[a]

	STEP 1						STEP 2				STEP 3			STEP 4		
	$R_fC_6H_4Br$[b]		n-BuLi		Et_2O	Time[e]	$B(OMe)_3$		Et_2O	Time[e]	HOAc		Time[e]	H_2O_2/H_2O[f]	Product	
Entry	g	mmol	mL	mmol	mL	min	g	mmol	mL	min	g	mmol	min	mL/mL	g	yield%
1	5.2	7.9	6	15.0	10[c] 40[d]	110	2.0	19	25	170	2.0	33	30	7/7	0.8	17.3
2	9.8	15.0	14	35.0	20[c] 80[d]	120	11.0	106	50	120	4.0	67	40	10/10	3.1	34.8
3	22.5	34.2	27	67.5	30[c] 150[d]	120	44.0	423	75	150	10.0	167	30	25/25	6.3	31.0
4	29.5	44.9	19	47.5	20[c] 125[d]	75	18.3	176	150	180	10.7	178	45	25/25	19.1	71.5
5	29.1	44.3	22	55.0	10[c] 150[d]	95	20.0	192	150	120	11.3	188	45	28/28	19.5	74.1
6	52.7	80.2	40	100.0	15[c] 225[d]	60	36.6	352	225	120	21.2	353	40	52/52	35.9	75.4

a) The reaction included four steps performed at -15 to -20°C; $R_fC_6H_4Br/Et_2O$ added to n-BuLi/Et_2O; the resultant solution (cold) added to $B(OMe)_3/Et_2O$ (via a double-tip needle) followed by treatments with HOAc and H_2O_2/H_2O.
b) $R_f = C_3F_7[OCF(CF_3)CF_2]_2$.
c) Ether admixed with $R_fC_6H_4Br$.
d) Ether added with n-BuLi.
e) The solution was stirred for the denoted period after addition of the reagent.
f) H_2O_2 : 30% concentration. The resultant reaction mixture was stirred at low temperature for 0.75 h, then at room temperature overnight.

$(C_6H_5O)_2P(O)Cl$ (0.95 g, 3.54 mmol), and benzene (5 mL) was added a solution of triethylamine (0.78 g, 7.7 mmol) in benzene (5 mL), over a period of 20 minutes. After stirring for an additional 0.5 h at room temperature, the reaction mixture was heated at 85°C for 20 h under nitrogen bypass. After cooling, the precipitated triethylamine hydrochloride was filtered off. Solvent removal from the filtrate followed by drying the residue in vacuo at 50-60°C resulted in a light yellow liquid (2.97 g, quantitative yield). The product was distilled in vacuo (<0.001 mm Hg) using a micro distillation apparatus (at an oil temperature of 145°C) to give 2.77 g of V (94.5% yield; GC purity >99%). The infrared spectrum is given in Figure 21, the TGA trace in Figure 22 and the mass spectrum in Table 26.

Preparation of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4OP(O)(C_6H_5)_2$ (VI)

In an inert atmosphere enclosure, to a solution of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4OH$ (2.00 g, 3.36 mmol), and $(C_6H_5)_2P(O)Cl$ (0.79 g, 3.34 mmol), in benzene (5 mL) was added a solution of triethylamine (0.68 g, 6.7 mmol) in benzene (5 mL), over a period of 20 minutes. Stirring at room temperature was continued for another 0.5 h, then the reaction mixture was heated at 85°C for 21 h under nitrogen bypass. After cooling, the precipitated triethylamine hydrochloride was removed by filtration in the inert atmosphere enclosure. Solvent removal from the filtrate followed by drying in vacuo at 60°C resulted in 2.69 g (quantitative yield) of an off-white solid. The product was

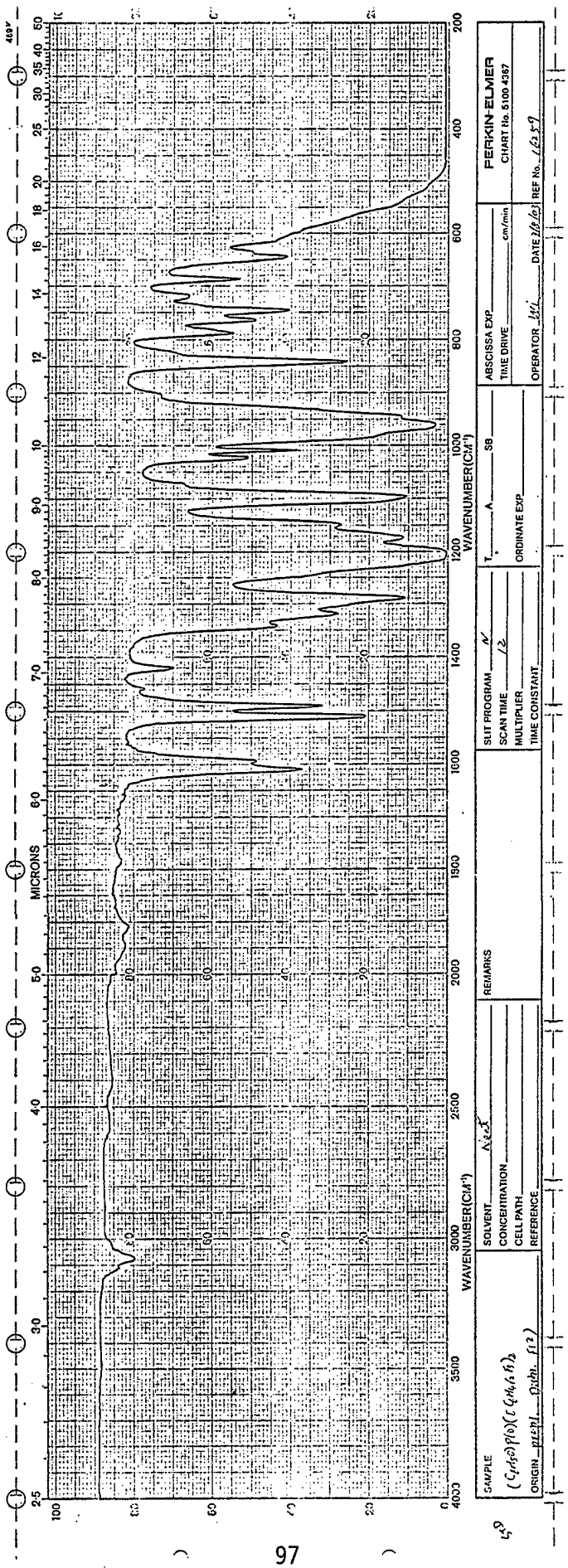


Figure 21. Infrared spectrum of $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OP(O)(OC_6H_5)_2$ (V).

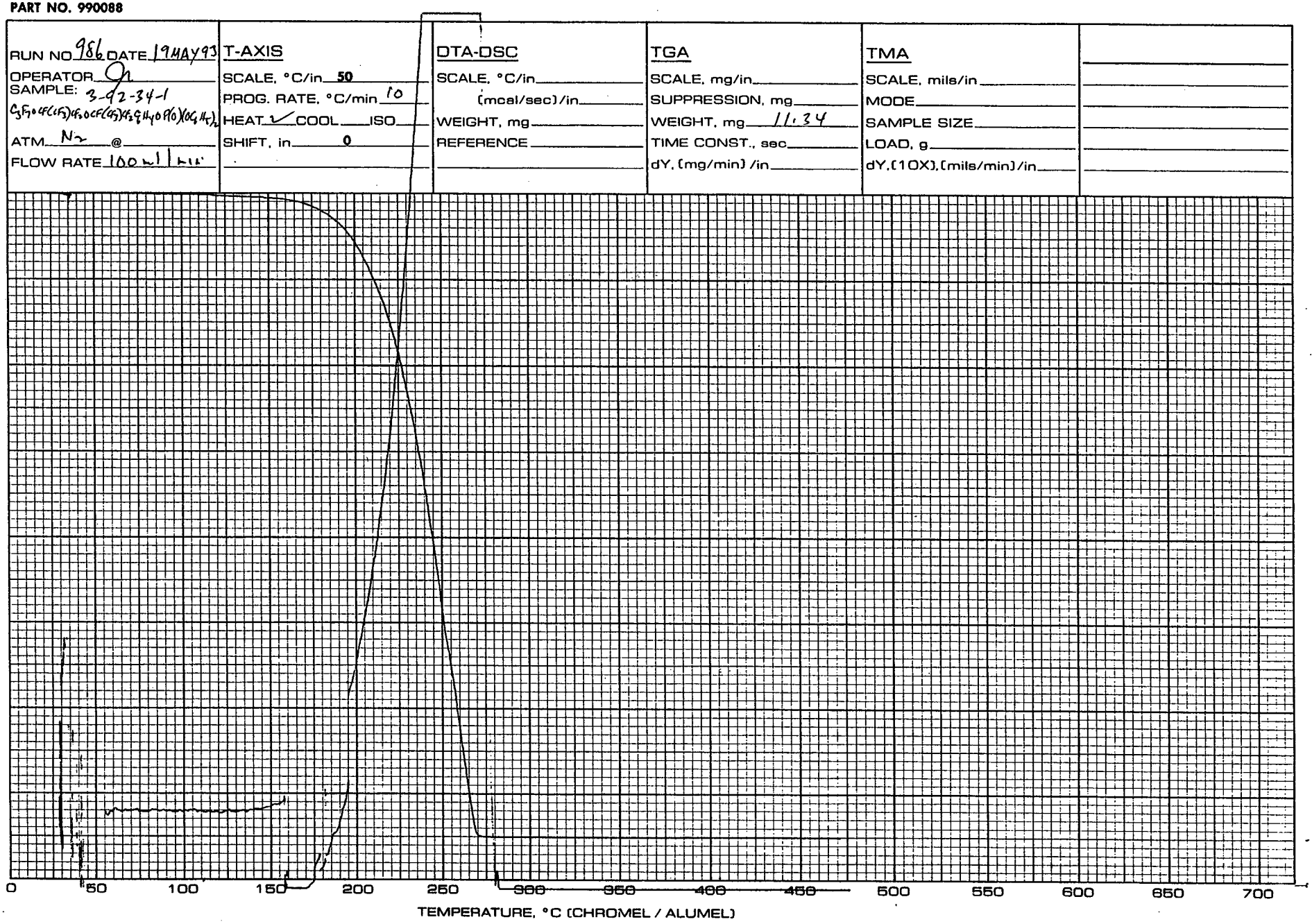


Figure 22. TGA of $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OP(O)(OC_6H_5)_2$ (V) in N_2.

TABLE 26

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF

$C_3F_7(OCF(CF_3)CF_2)_2C_6H_4OP(O)(OC_6H_5)_2$ (MW 826)

m/e	%	m/e	%	m/e	%	m/e	%
31	26.9	81	6.2	143	35.3	218	6.0
32	4.3	88	3.6	144	4.2	219	23.9
38	6.3	92	3.4	145	11.3	220	4.1
39	31.8	93	20.3	150	9.2	232	3.8
40	3.3	94	20.3	151	3.5	233	17.8
47	38.4	95	4.6	152	6.5	234	3.1
50	33.7	96	4.1	153	5.3	281	7.3
51	32.1	97	6.2	156	7.3	373	3.4
52	3.5	100	24.1	168	11.0	375	100.0
62	3.8	114	11.0	169	38.2	376	37.5
63	13.2	115	3.5	170	9.7	377	7.0
64	6.6	119	18.0	171	4.5	475	10.0
65	42.1	125	4.0	188	32.5	541	3.2
66	15.8	126	8.7	189	13.4	707	6.3
69	83.0	127	9.2	203	6.6	807	11.6
74	3.8	131	8.3	205	19.8	808	3.8
75	7.2	139	11.7	212	3.3	825	32.9
76	7.9	140	23.0	215	23.2	826	65.4M^+
77	81.7	141	7.8	216	3.8	827	29.0
78	17.7	142	7.8	217	8.0	828	5.9

Peaks having intensities lower than 3% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e		m/e	
826	M^+	233	$OP(OC_6H_5)_2^+$
807	$[M - F]^+$	188	$CF_2C_6H_3OPO^+$
707	$[M - C_2F_5]^+$	169	$C_3F_7^+$
475	$[M - C_3F_7OCF(CF_3)CF_2O]^+$	143	$FPOC_6H_5^+$, $CF_2C_6H_4OH^+$
375	$[M - C_3F_7OCF(CF_3)CF_2OCF(CF_3)]^+$		

recrystallized from hexanes (12 mL) to yield a 2.00 g (75% yield) of VI as a white solid, MP 67-70°C (GC purity 98%). The infrared spectrum is given in Figure 23, the TGA trace in Figure 24 and the mass spectrum in Table 27.

Preparation of $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)OC_6H_5$ (VII)

In an inert atmosphere enclosure into a stirred solution of $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OH$ (19.0 g, 32.0 mmol) and $C_6H_5OP(O)Cl_2$ (3.5 g, 16.0 mmol) in Freon-113 (60 mL) was added triethylamine (6.6 g, 65 mmol) in benzene (40 mL) over a period of 1 h. Stirring at room temperature was continued for an additional 0.5 h, then the reaction mixture was heated at 65°C (under nitrogen bypass) for 20 h. After cooling, the precipitated triethylamine hydrochloride was filtered in an inert atmosphere enclosure and rinsed with Freon-113 (10 mL) and benzene (5 mL). The filtrate, following solvent evaporation in vacuo, gave 21.2 g of light brown liquid which was mixed with 10% ether/hexanes (6 mL) and passed through a silica gel column (100g, 45 cm x 2.5 cm, packed in 10% ether/hexanes). Elution using 750 mL of 10% ether/hexanes resulted in the recovery of 18.4 g of clear, colorless product. The remaining impurities were sublimed off (at 70-80°C for 4 h, 85-90°C for 4 h, then at 90-95°C for 3 h) to give 16.7 g (78.7% yield) of $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)OC_6H_5$ (GC purity 99%). The infrared spectrum is given in Figure 25, the mass spectrum in Table 28 and the TGA trace in Figure 26.

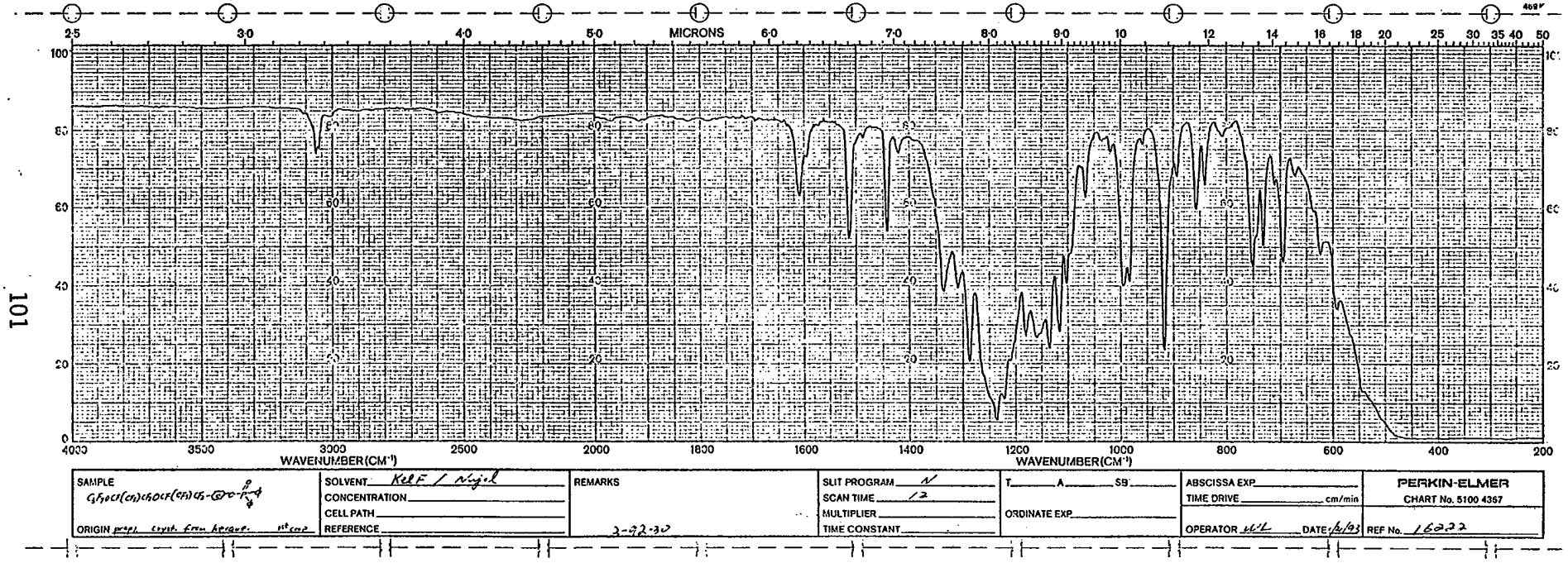


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Figure 23. Infrared spectrum of $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OP(O)(C_6H_5)_2$ (VI).

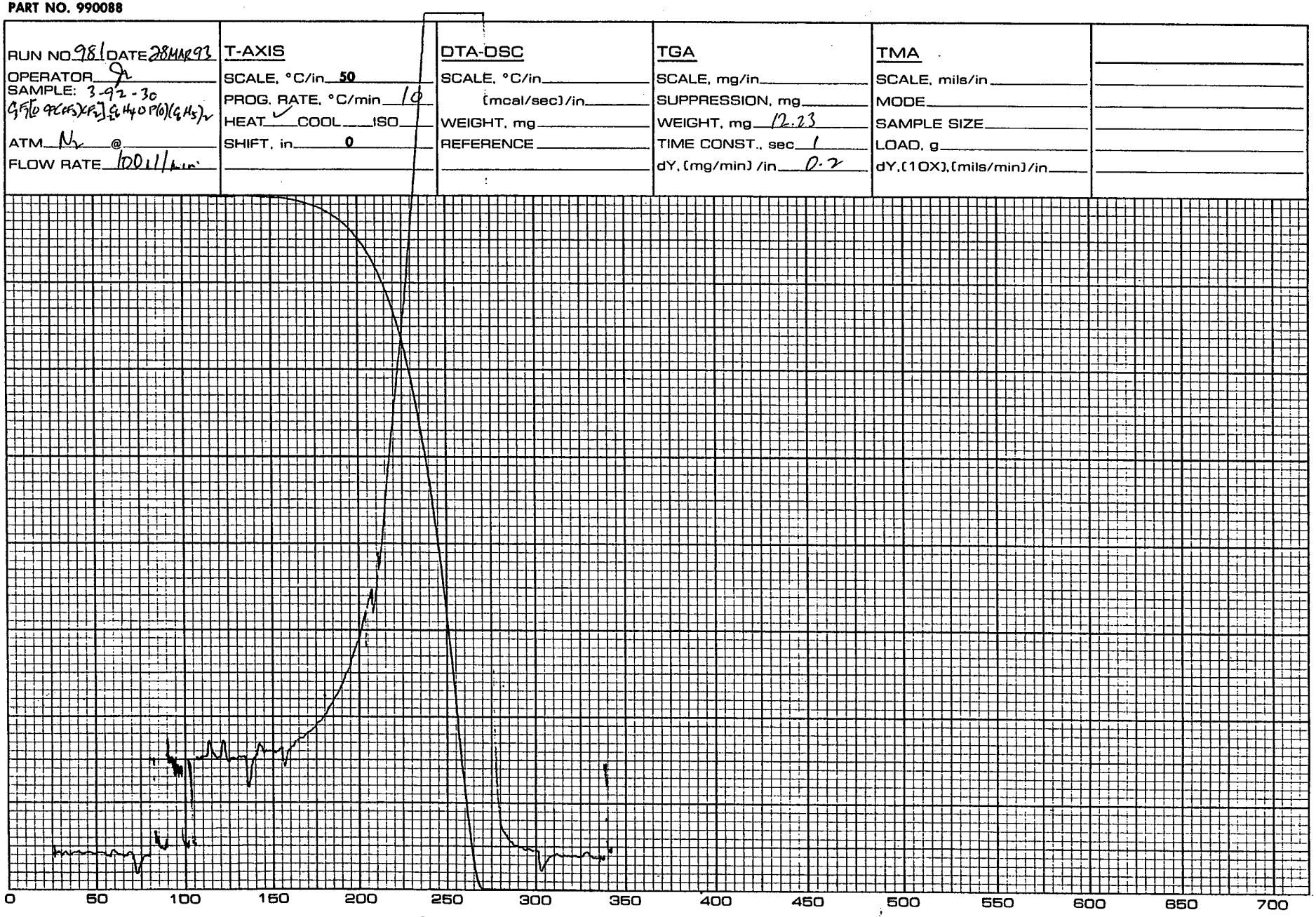


Figure 24. TGA of $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OP(O)(C_6H_5)_2$ (VI) in N_2.

TABLE 27

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF

$C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OP(O)(C_6H_5)_2$ (MW 794)

m/e	%	m/e	%	m/e	%	m/e	%
31	13.7	88	2.1	143	13.5	200	3.4
32	2.8	95	6.1	145	5.1	201	100.0
38	2.8	97	2.1	147	2.7	202	28.3
39	4.0	100	6.5	150	2.5	203	4.7
47	22.6	107	2.7	152	5.6	219	8.1
50	14.9	114	10.3	153	4.3	220	3.1
51	27.1	115	2.1	154	3.8	343	11.0
52	2.5	119	7.7	169	17.1	344	2.6
63	3.1	123	3.4	170	2.1	443	2.7
66	2.2	125	3.2	171	7.1	775	3.3
69	42.0	126	3.3	172	5.8	793	21.1
75	3.4	127	3.3	173	3.5	794	22.6M^+
76	2.8	128	3.0	183	4.1	795	6.2
77	41.3	141	2.0	189	2.0		
78	8.4	142	5.3	199	5.0		

Peaks having intensities lower than 2% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e

794 - M^+

775 - $[M - F]^+$

343 - $CF_2C_6H_4OP(O)(C_6H_5)_2^+$

201 - $OP(O)(C_6H_5)_2^+$

169 - $C_3F_7^+$

143 - $CF_2C_6H_4OH^+$

77 - $C_6H_5^+$

69 - CF_3^+

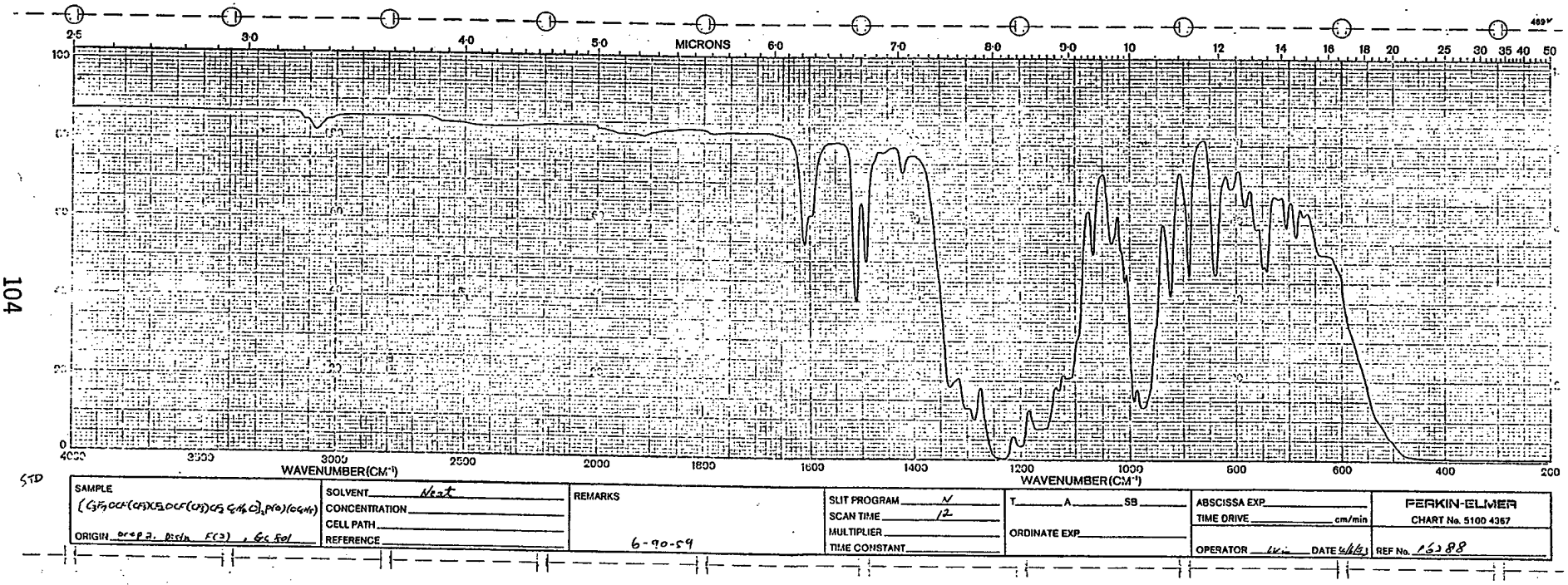


Figure 25. Infrared spectrum of $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)OC_6H_5$ (VII).

TABLE 28

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF

$[C_3F_7(OCF(CF_3)CF_2)_2C_6H_4O]_2P(O)OC_6H_5$ (MW 1326)

m/e	%	m/e	%	m/e	%	m/e	%
31	8.8	93	6.1	145	18.6	263	6.5
39	5.4	94	6.2	150	10.8	301	5.8
47	10.5	96	3.4	169	17.1	375	4.2
50	14.0	97	4.6	189	12.2	826	5.2
51	8.8	100	15.9	195	3.1	873	3.9
57	3.0	114	9.6	203	7.9	875	74.9
63	7.2	119	26.6	205	15.5	876	31.4
64	3.8	125	5.2	211	3.8	877	11.0
65	19.1	126	10.5	212	46.3	935	3.2
66	12.2	127	8.6	213	21.9	975	17.0
67	4.9	131	4.7	214	3.3	976	6.0
69	100.0	139	3.1	217	7.6	1041	15.8
75	4.7	140	9.7	218	3.5	1042	4.4
77	28.6	141	3.2	219	11.9	1207	16.5
78	6.4	142	4.5	237	3.3	1326	30.7M^+
81	3.9	143	16.3	262	12.9	1327	12.7

Peaks having intensities lower than 3% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e

1326 - M^+

1207 - $[M - C_2F_5]^+$

1041 - $[M - C_3F_7OCF(CF_3)]^+$

975 - $[M - C_3F_7OCF(CF_3)CF_2O]^+$

875 - $[M - C_3F_7OCF(CF_3)CF_2OCF(CF_3)]^+$

212 - $CF_3CF_2C_6H_4OH^+$

205 - $CF_2C_6H_4OPO_2^+$

189 - $CF_2C_6H_4OPO^+$

169 - $C_3F_7^+$

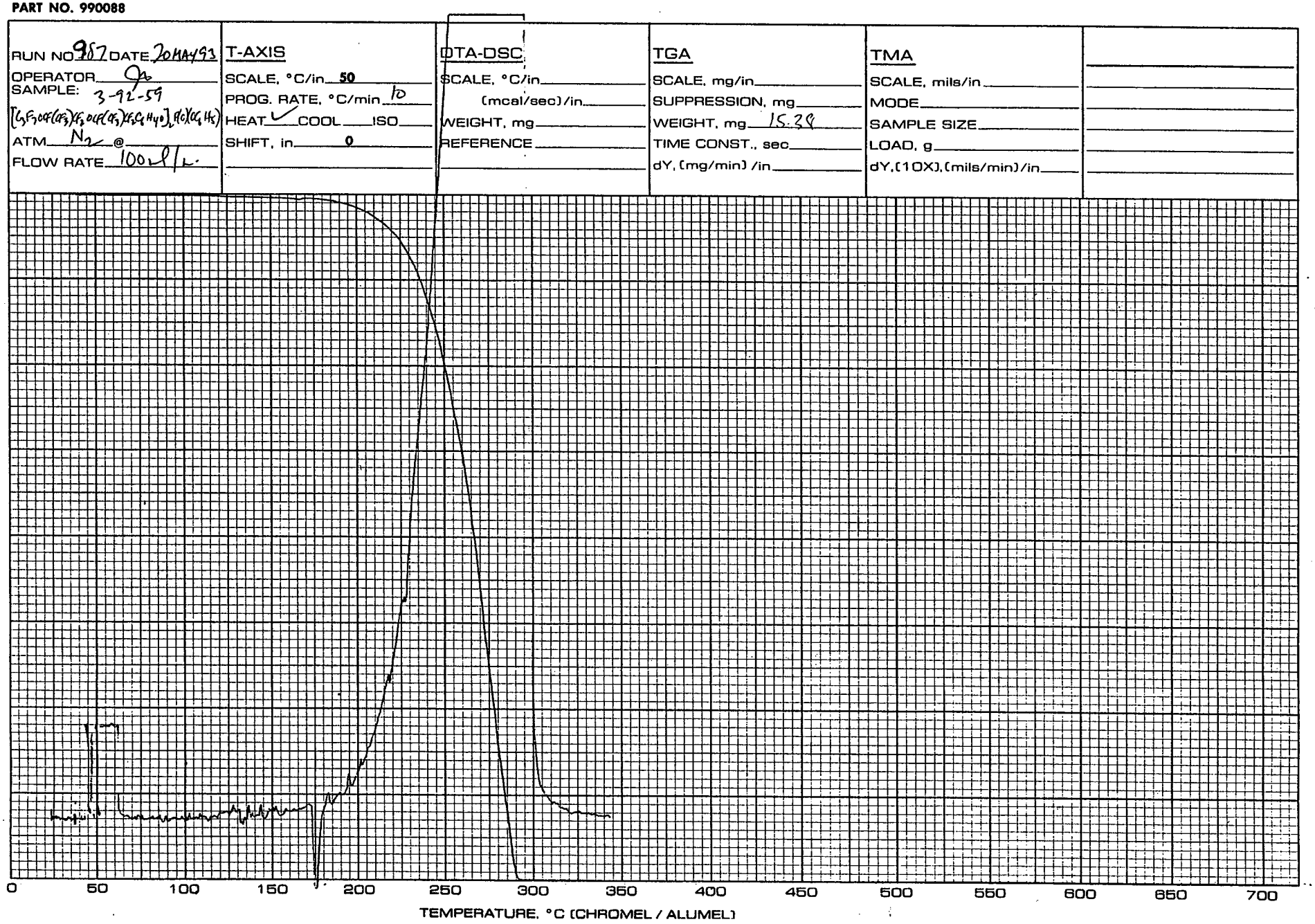


Figure 26. TGA of $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)OC_6H_5$ (VII).

Preparation of $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)C_6H_5$ (VIII)

In an inert atmosphere enclosure into a stirred solution of $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OH$ (33.04 g, 55.60 mmol) and $C_6H_5P(O)Cl_2$ (5.58 g, 28.6 mmol) in Freon-113 (110 mL) and benzene (25 mL) was added triethylamine (11.2 g, 111 mmol) in benzene (35 mL) over a period of 1.5 h. Stirring at room temperature was continued for additional 0.75 h; then the reaction mixture was heated at 65°C under nitrogen bypass for 44 h. After cooling, the precipitated triethylamine hydrochloride was filtered off. Solvent evaporation from the filtrate gave 36.7 g of yellow liquid which was purified using a silica gel column (150 g, 41 cm x 3 cm, packed in 10% ether/hexanes) and elution with 10% (400 mL) and 20% (600 mL) of ether/hexanes. No phosphonate was present in the first 475 mL. In the next 500 mL of the eluent 30.7 g of a clear, colorless liquid was obtained. This was further purified by removing the remaining impurities by sublimation at 65-85°C to give 28.7 g (78.7% yield) of $\{C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O\}_2P(O)C_6H_5$ (GC purity > 99%). The infrared spectrum is given in Figure 27, the TGA trace in Figure 28 and the mass spectrum in Table 29.

Preparation of $C_3F_7[OCF(CF_3)CF_2]_3OCF(CF3)C(O)C_6H_4Br$

To 1,4-dibromobenzene (20.2 g, 85.6 mmol) in freshly distilled ether (175 mL) was added n-butyllithium (2.5 M in hexanes, 44 mL, 110 mmol) at -78°C, over a period of 25 minutes. After stirring at -30 to -40°C for 3 h, the solution was cooled back to -78°C and C3F7[OCF(CF3)CF2]3OCF(CF3)CO2Me (70.0 g, 83.1

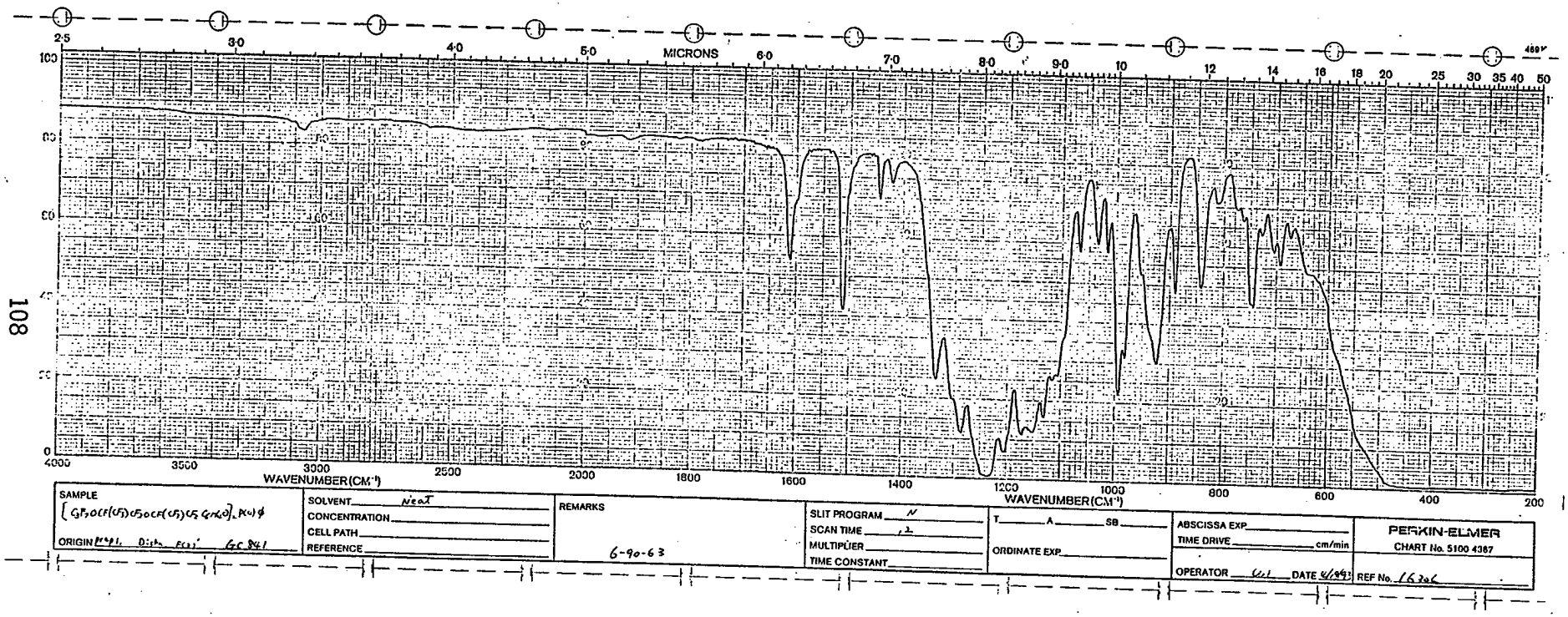


Figure 27. Infrared spectrum of $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)C_6H_5$ (VIII).

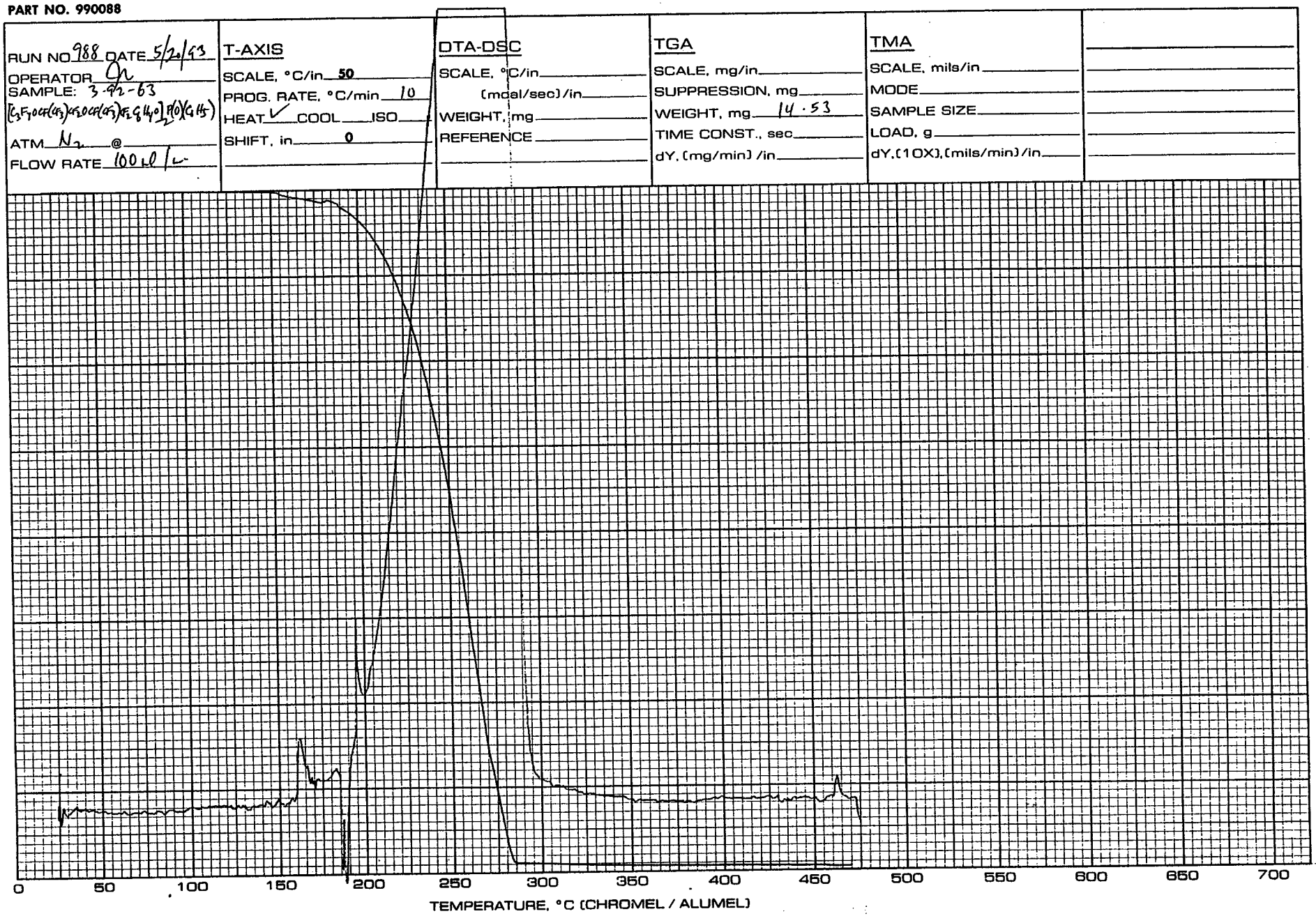


Figure 28. TGA of $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)C_6H_5$ (VIII) in N_2.

TABLE 29

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF

$[C_3F_7(OCF(CF_3)CF_2)_2C_6H_4O]_2P(O)C_6H_5$ (MW 1310)

m/e	%	m/e	%	m/e	%	m/e	%	m/e	%
31	42.0	95	5.5	151	3.0	220	4.2	347	3.1
35	2.0	96	5.9	157	3.3	223	3.7	363	2.6
36	13.7	97	12.7	161	6.9	225	3.7	365	4.0
38	10.8	100	33.7	162	5.3	226	2.4	366	2.0
39	5.7	101	2.2	163	3.2	227	2.9	381	3.1
47	39.9	107	4.5	164	3.6	229	5.9	385	8.4
50	38.5	112	2.6	165	7.9	243	3.1	481	4.6
51	18.5	113	3.9	169	47.7	245	3.5	551	7.8
57	2.6	114	19.2	170	3.9	254	13.5	552	2.0
62	4.4	115	2.9	173	3.6	255	4.2	594	2.7
63	8.2	119	32.2	175	2.3	263	2.1	670	6.8
64	3.1	123	2.2	176	4.9	265	7.2	671	2.7
65	3.0	124	7.2	189	21.5	266	3.5	716	3.4
66	12.9	125	8.2	190	3.5	267	2.4	717	4.7
67	3.1	126	26.7	192	2.0	269	3.1	719	5.1
69	100.0	127	16.7	193	3.2	283	3.5	736	2.3
70	4.7	128	3.2	195	9.1	285	27.0	739	2.3
74	3.8	131	11.4	201	2.8	286	6.5	857	6.9
75	8.9	133	3.6	203	11.5	289	2.1	859	82.4
76	6.9	141	6.1	204	56.5	297	3.0	860	32.1
77	37.6	142	11.3	205	21.8	301	2.1	861	8.6
78	15.7	143	65.2	207	2.5	303	2.7	939	2.0
81	7.6	144	10.1	211	2.7	313	3.9	959	18.0
85	5.7	145	34.3	213	3.1	335	13.6	960	4.8
88	7.9	146	4.9	214	3.4	336	2.1	1025	11.4
93	3.7	147	6.2	217	4.4	337	3.0	1026	3.8
94	2.5	150	20.0	219	15.7	345	5.8	1191	17.6
								1310	35.6M+
								1311	14.0

Peaks having intensities lower than 2% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e		m/e	
1310	- M^+	285	- $C_3F_7OCFCF_3^+$
1191	- $[M - C_2F_5]^+$	204	- $CF_2C_6H_3OP(O)_2^+$
1025	- $[M - C_3F_7OCFCF_3]^+$	169	- $C_3F_7^+$
959	- $[M - C_3F_7OCF(CF_3)CF_2O]^+$	143	- $CF_2C_6H_4OH^+$
859	- $[M - C_3F_7OCF(CF_3)CF_2OCFCF_3]^+$	69	- CF_3^+

mmol) in ether (50 mL) was added over 0.5 h. Stirring was continued for additional 1.5 h at -78°C. Subsequently, hydrochloric acid (2N, 120 mL) was added while the solution was slowly warmed up to room temperature. The resultant mixture was stirred at room temperature overnight. The organic layer (golden yellow) was separated and combined with the ether extract (50 mL) of the aqueous layer. The combined ethereal solution was washed with water (4 x 50 mL) and dried over anhydrous MgSO4. Solvent removal, followed by distillation, gave 48.0 g (59.7% yield) of light yellow liquid $C_3F_7[OCF(CF_3)CF_2]_3OCF(CF_3)C(O)C_6H_4Br$, BP 87-90°C/0.001 mm Hg (GC purity 97%). The infrared and mass spectra are given in Figure 29 and Table 30, respectively.

Preparation of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4Br$

Into a Parr bomb (125 mL), cooled in Dry Ice containing $C_3F_7[OCF(CF_3)CF_2]_3OCF(CF_3)C(O)C_6H_4Br$ (48.0 g, 49.6 mmol) and Freon-113 (20 mL) was added under nitrogen flow, anhydrous hydrogen fluoride (approximately 5 mL). Subsequently, sulfur tetrafluoride (15.0 g, 139 mmol) was condensed in. After warming to room temperature, the bomb was agitated, using a shaker assembly, at 100-110°C (sand bath) for 20 h. Following cooling to room temperature and venting, Freon-113 (25 mL) was added to the contents which were then poured onto ice-water (100 mL). The reactor was rinsed with additional quantity of Freon-113 (25 mL). The combined organic layer was washed with a saturated sodium bicarbonate (3 x 50 mL,), water (3 x 25 mL), and dried over

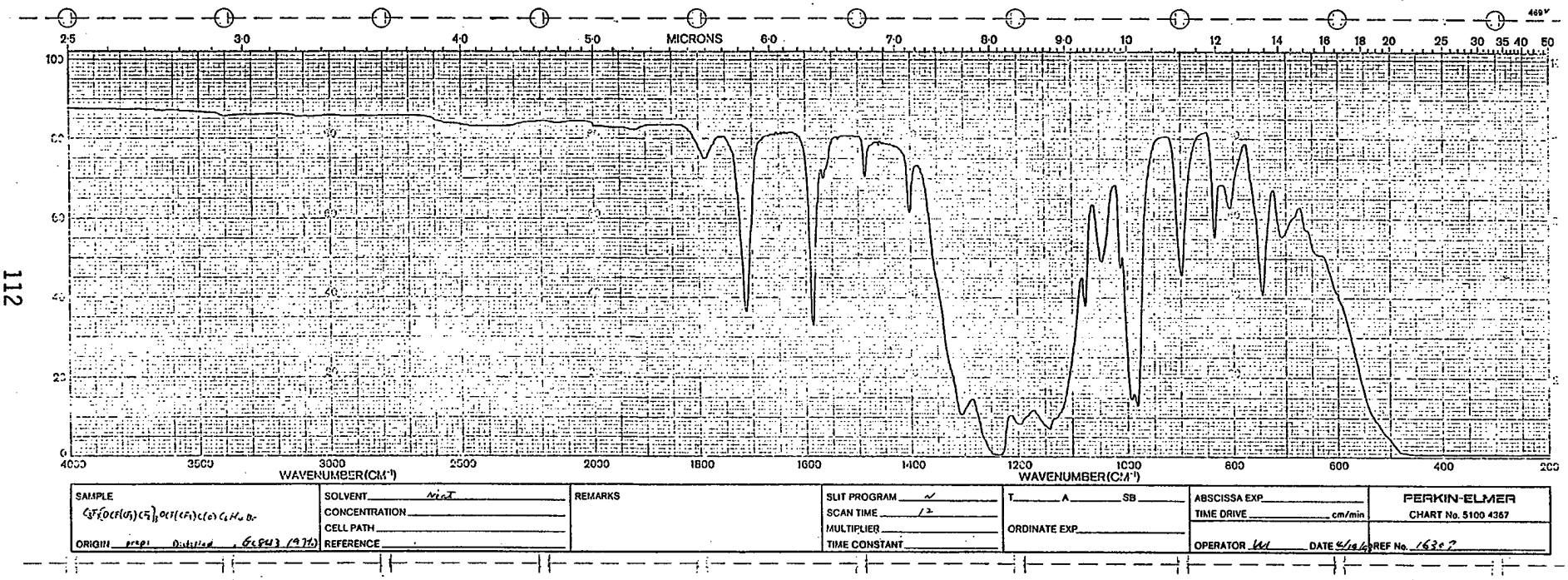


Figure 29. Infrared spectrum of $C_3F_7[OCF(CF_3)CF_2]_3OCF(CF_3)C(O)C_6H_4Br$.

TABLE 30

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF

$C_3F_7[OCF(CF_3)CF_2]_3OCF(CF_3)C(O)C_6H_4Br$ (MW 966)

m/e	%	m/e	%	m/e	%	m/e	%
31	19.3	80	3.2	155	28.5	207	6.0
38	3.3	81	7.2	156	4.9	255	13.9
47	15.4	82	3.4	157	28.8	257	13.1
50	33.7	95	5.7	158	4.1	283	3.7
51	6.8	97	10.3	169	38.7	285	4.1
66	4.7	100	22.4	176	4.9	335	6.9
69	59.5	104	16.6	183	97.6	349	3.6
74	9.3	105	9.5	184	16.3	351	3.7
75	25.1	119	18.5	185	100.0	449	10.5
76	31.5	123	4.2	186	15.4	451	10.2
77	7.5	131	9.9	202	3.5	615	4.2
78	3.7	147	11.8	204	6.8	617	4.4
79	3.5	150	22.5	205	6.6	947	4.5
						949	5.5

Peaks having intensities lower than 3% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition (only ions having ^{79}Br isotope are listed)

m/e

947 - $[M - F]^+$

615 - $[M - F(C_3F_6O)_2]^+$

449 - $[M - F(C_3F_6O)_3]^+$

183 - $BrC_6H_4CO^+$

155 - $BrC_6H_4^+$

69 - CF_3^+

anhydrous $MgSO_4$. Solvent removal resulted in 42.7 g of product (GC purity 97%). Distillation gave 39.6 g (81.0% yield) of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4Br$, BP 78-80°C/0.001 mm Hg (GC purity > 99%). Its infrared and mass spectra are given in Figure 30 and Table 31, respectively.

Typical Preparation of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OH$

Under nitrogen bypass, to n-butyllithium (7.0 mL, 2.5 M in hexanes, 17.5 mmol) and diethyl ether (80 mL) at -10 to -15°C, was added $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4Br$ (9.94 g, 10.1 mmol) in diethyl ether (20 mL) over a period of 30 minutes. Stirring was continued for additional 2 h at -10 to -15°C, then the cold (orange-brown) solution was added over 0.5 h (via a double-tip needle) at -10 to -15°C to trimethyl borate (5.58 g, 53.7 mmol; distilled over sodium) in ether (50 mL). After 2 h, acetic acid (3.0 g, 50 mmol) was introduced and the solution stirred for an additional 1 h. Then at -10 to -15°C was added hydrogen peroxide (30%, 7.5 mL, 74.0 mmol, in H_2O 8.5 mL). The reaction mixture was subsequently stirred at room temperature overnight. This was followed by the addition of water (50 mL). The organic layer was separated, combined with ether extract (50 mL) of the aqueous layer, washed with ferrous sulfate solution (10 g $FeSO_4.7H_2O$, 4 mL concentrated hydrochloric acid, 10 mL H_2O), water, and dried over anhydrous $MgSO_4$. After solvent evaporation <u>in vacuo</u> 7.6 g (82% yield) of brown liquid was obtained which was purified by passing through a silica gel column (70 g, 2.5 cm x 29 cm, packed in 5%

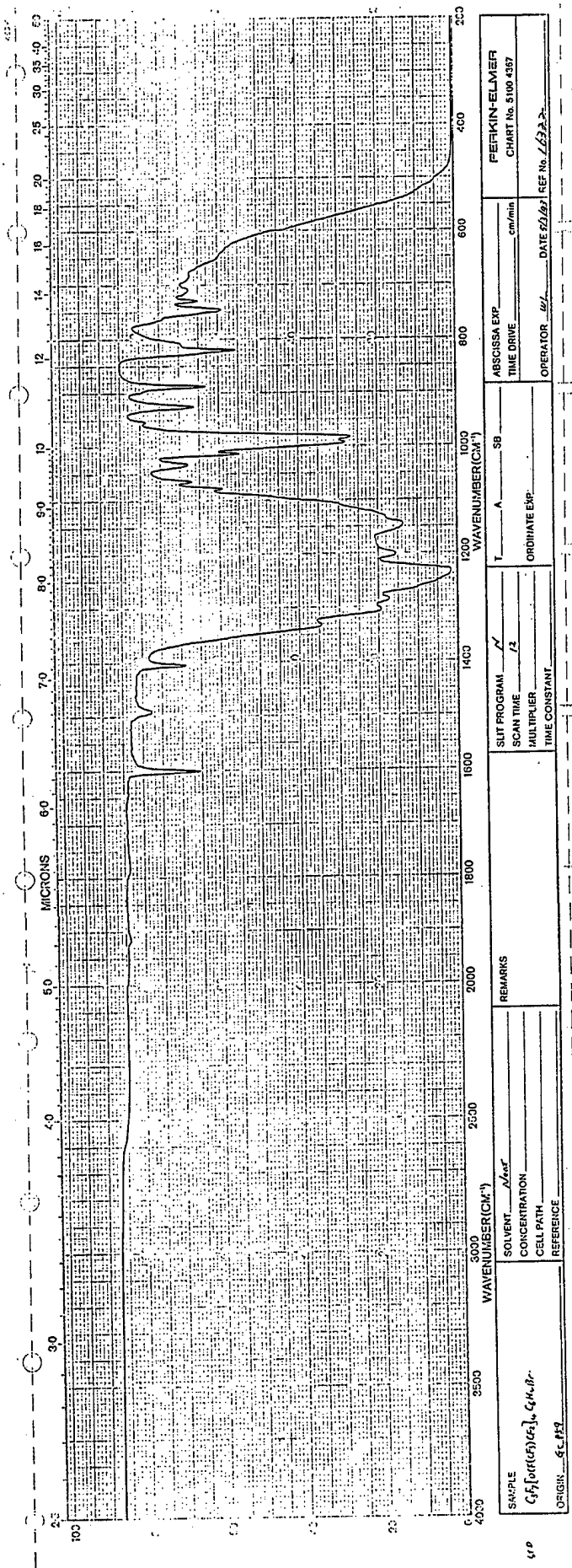


Figure 30. Infrared spectrum of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4Br$.

TABLE 31

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF

$C_3F_7[OCF(CF_3)CF_2]_4C_6H_4Br$ (MW 988)

m/e	%	m/e	%	m/e	%	m/e	%
31	23.2	105	2.2	187	2.1	304	4.7
38	3.5	106	3.0	195	10.1	305	28.8
39	3.4	107	9.9	204	4.8	306	7.4
47	19.5	114	2.4	205	100.0	307	30.4
50	27.8	119	24.5	206	24.3	308	7.7
51	8.2	125	17.6	207	98.4	313	3.4
57	3.9	126	39.4	208	22.1	335	14.7
62	5.2	127	21.8	213	2.0	372	3.0
63	3.2	128	5.2	223	4.7	373	3.6
66	7.0	131	13.4	224	5.0	401	2.9
69	82.1	137	4.4	225	7.6	403	2.8
70	4.7	138	4.3	226	15.0	471	11.0
74	8.3	144	3.3	227	5.8	472	2.5
75	18.1	145	16.9	233	2.0	473	11.0
76	11.7	146	3.0	235	3.3	474	2.2
77	3.4	147	21.9	236	7.4	501	2.0
78	5.9	150	23.7	238	6.7	637	2.2
79	5.8	151	3.6	245	7.4	703	6.5
80	6.1	155	3.0	255	17.3	705	6.1
81	13.2	156	4.0	256	3.5	869	4.3
82	4.7	157	9.6	257	16.8	871	3.8
87	3.3	158	2.9	258	2.6	969	8.4
88	2.2	160	2.2	273	2.5	971	10.9
93	3.8	169	76.2	275	2.3	988	29.3
95	3.4	170	7.1	285	9.4	990	37.6
97	16.2	173	2.0	286	3.4	991	8.5
99	4.7	175	2.6	287	7.1		
100	28.3	176	8.9	288	2.9		
101	2.6	177	2.7	302	4.5		

Peaks having intensities lower than 2% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition
(only ions having ^{79}Br isotope are listed)

m/e
988 - M^+
969 - $[M - F]^+$
869 - $[M - C_2F_5]^+$
637 - $[M - F(C_3F_6O)_2]^+$
471 - $[M - F(C_3F_6O)_3]^+$
335 - $C_3F_7OCF(CF_3)CF_2^+$

m/e
305 - $[M - F(C_3F_6O)_4]^+$
255 - $BrC_6H_4CF_2CF_2^+$
205 - $BrC_6H_4CF_2^+$
169 - $C_3F_7^+$
126 - $CF_2C_6H_4^+$

ether/hexanes). The first yellow band (2.21 g) eluted with 170 mL of 5% ether/hexanes, consisted of 74% (by GC) of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_5$. The second yellow band (5.98 g) eluted with 140 mL of 20% and 170 mL of 1:1 ether/hexanes, consisted of 96% of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OH$. The purified products from three preparations were combined (total weight 17.4 g) and distilled to give 14.4 g of clear colorless $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OH$, BP 86-88°C/0.001 mm Hg (GC purity >99%). The average yield was 40% based on the bromide employed. The mass spectrum of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_5$ is given in Table 32. The mass and infrared spectra of the phenol are presented in Table 33 and Figure 31, respectively.

Preparation of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OP(O)(C_6H_5)_2$ (IX)

In an inert atmosphere enclosure into a stirred solution of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OH$ (2.00 g, 2.16 mmol) and $ClP(O)(C_6H_5)_2$ (0.51 g, 2.16 mmol) in benzene was added triethylamine (0.69 g, 6.82 mmol) in Freon-113 (5 mL) over a period of 0.5 h. Stirring was continued for an additional 0.5 h, then the reaction mixture was heated at 60°C under nitrogen bypass for 67 h. After cooling, the precipitated triethylamine hydrochloride was filtered off in an inert atmosphere enclosure and rinsed with Freon-113 (3 mL) and benzene (6 mL). Solvent evaporation in vacuo gave 2.43 g of a viscous liquid product (which turned into a waxy solid on standing overnight). This material was mixed with 10% ether/hexanes (5 mL) and passed through a silica gel column (35 g, 26.5 cm x 2.2 cm,

TABLE 32

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF

$C_3F_7[OCF(CF_3)CF_2]_4C_6H_5$ (MW 910)

m/e	%	m/e	%	m/e	%	m/e	%
31	16.5	97	9.3	155	3.8	293	2.0
39	3.2	100	19.3	157	2.4	295	2.2
47	13.5	101	3.4	158	7.1	323	4.5
50	18.4	107	4.2	169	49.9	335	9.4
51	11.1	108	2.7	170	4.0	373	3.4
57	2.2	119	18.6	176	2.6	393	15.1
62	2.0	125	3.8	177	21.0	394	3.1
63	2.0	126	8.5	178	3.9	625	9.5
66	4.7	127	100.0	187	2.4	626	2.5
69	60.9	128	28.1	189	2.7	771	2.2
70	3.0	129	2.5	195	3.8	791	5.7
74	2.3	131	8.3	205	2.4	871	2.1
75	5.3	138	2.2	207	20.7	891	10.1
76	2.8	145	9.1	208	5.5	892	3.1
77	18.5	146	5.5	224	3.5	910	15.3M^+
78	5.1	147	13.1	227	56.7	911	4.5
81	5.2	150	18.2	228	10.2		
96	4.8	151	2.0	245	2.6		

Peaks having intensities lower than 2% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e

910 - M^+

891 - $[M - 19]^+$

625 - $[M - C_3F_7OCF(CF_3)]^+$

393 - $CF(CF_3)CF_2OCF(CF_3)CF_2C_6H_5^+$

227 - $CF(CF_3)CF_2C_6H_5^+$

127 - $CF_2C_6H_5^+$

TABLE 33

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF

$C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OH$ (MW 926)

m/e	%	m/e	%	m/e	%	m/e	%
31	24.2	100	36.3	170	6.5	309	3.2
39	4.8	101	2.7	171	2.2	313	7.0
43	3.6	112	2.2	173	3.7	335	13.0
47	25.0	113	3.0	174	4.9	339	3.9
50	25.6	114	10.0	175	2.4	389	2.2
51	4.3	119	42.9	176	2.0	409	8.1
56	2.3	120	2.2	192	3.5	475	3.6
57	2.5	123	2.7	193	18.8	501	2.0
62	2.4	125	2.8	194	3.7	575	2.2
63	3.7	128	3.3	195	5.5	621	5.1
65	4.6	131	10.7	211	2.9	641	5.5
66	4.1	141	3.1	213	3.6	787	3.9
67	2.6	142	7.3	214	9.7	806	2.8
69	83.6	143	100.0	220	2.1	857	2.0
70	2.7	144	19.0	223	16.3	887	4.7
71	2.9	145	20.6	224	2.0	906	7.0
75	4.4	146	2.3	239	2.5	907	13.2
78	7.3	147	20.4	242	2.4	908	3.6
81	7.5	150	37.7	243	27.7	909	3.2
88	2.4	151	5.2	244	4.4	925	2.1
89	2.8	161	8.7	245	4.2	926	17.7M^+
93	3.5	163	3.5	261	2.1	927	4.5
95	6.2	164	2.5	285	3.0		
97	18.5	169	62.2	289	2.1		

Peaks having intensities lower than 2% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e		m/e	
926	M^+	193	$C_2F_4C_6H_4OH^+$
907	$[M - F]^+$	169	$C_3F_7^+$
906	$[M - HF]^+$	143	$CF_2C_6H_4OH^+$
335	$C_3F_7OCF(CF_3)CF_2^+$	119	$C_2F_5^+$
243	$CF(CF_3)CF_2C_6H_4OH^+$	69	CF_3^+

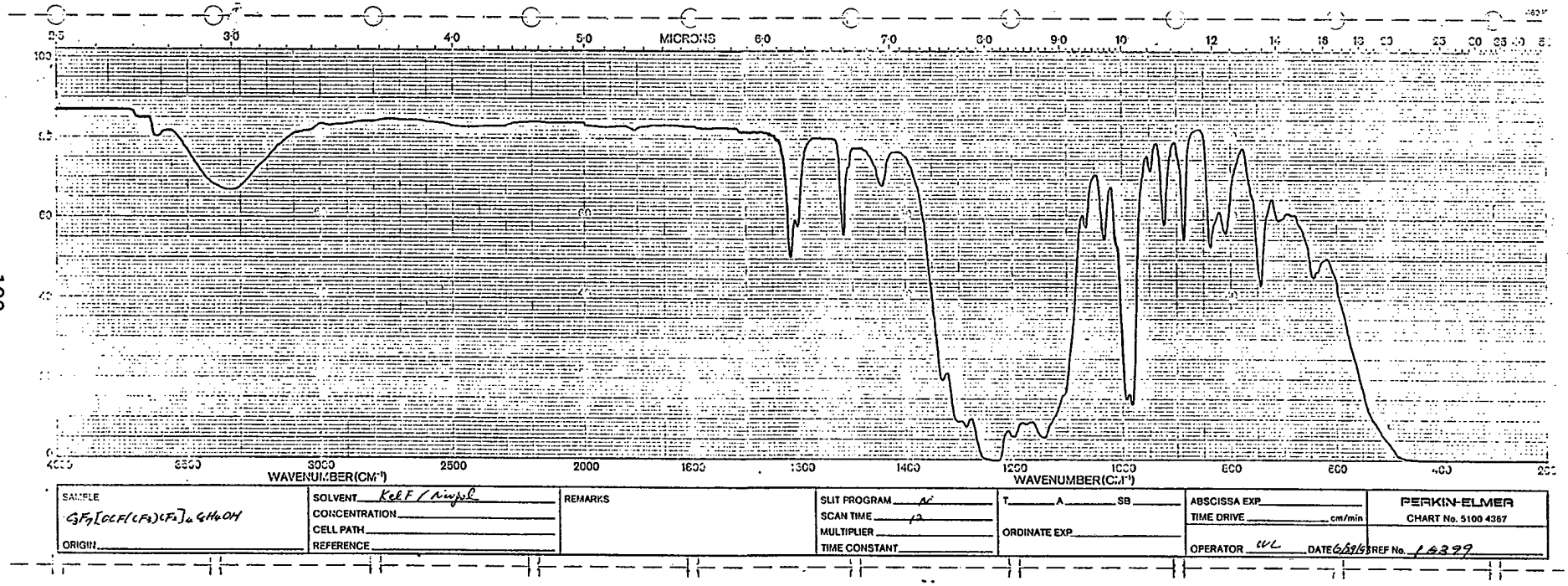


Figure 31. Infrared spectrum of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OH$.

packed with 10% ether/hexanes). The column was eluted with 10% ether/hexanes (235 mL), 20% (250 mL) and 30% (250 mL). A colored band remained at the top of the column and fractions were collected in 50 mL aliquots. Fractions 3-11 contained 0.64 g of material which was mainly unreacted phenol; fraction 12, 0.65 g a colorless viscous liquid (GC purity 96%); fraction 13, 0.87 g of a white waxy solid (98% GC purity); and fraction 14, 0.24 g of a colorless viscous liquid (GC purity 0.86%), for a total of 2.40 g (99% recovery). Fractions 12 and 14 in 10% ether/hexanes (5 mL) were again passed through a silica gel column (10 g, 17 cm x 1.6 cm, packed with 10% ether/hexanes). Elution with 10% ether/hexanes (165 mL) and 20% (150 mL) resulted in the isolation of another 250 mg of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OP(O)(C_6H_5)_2$ (GC purity >99%), bringing the total to 1.11 g (yield 45.6%). The infrared spectrum is given in Figure 32, the mass spectrum in Table 34 and the TGA trace in Figure 33.

Preparation of $\{C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O\}_2P(O)(C_6H_5)$ (X)

In an inert atmosphere enclosure into a stirred solution of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OH$ (3.00 g, 3.24 mmol) and $C_6H_5P(O)Cl_2$ (0.30 g, 1.54 mmol) in benzene (7 mL) and Freon-113 (3 mL) was added triethylamine (1.71 g, 16.9 mmol) in Freon-113 (10 mL) over a period of 40 minutes. Stirring was continued for additional 0.5 h at room temperature, then the reaction mixture was heated at 60°C under nitrogen bypass for 93 h. After cooling, the precipitated triethylamine hydrochloride was filtered off in an inert

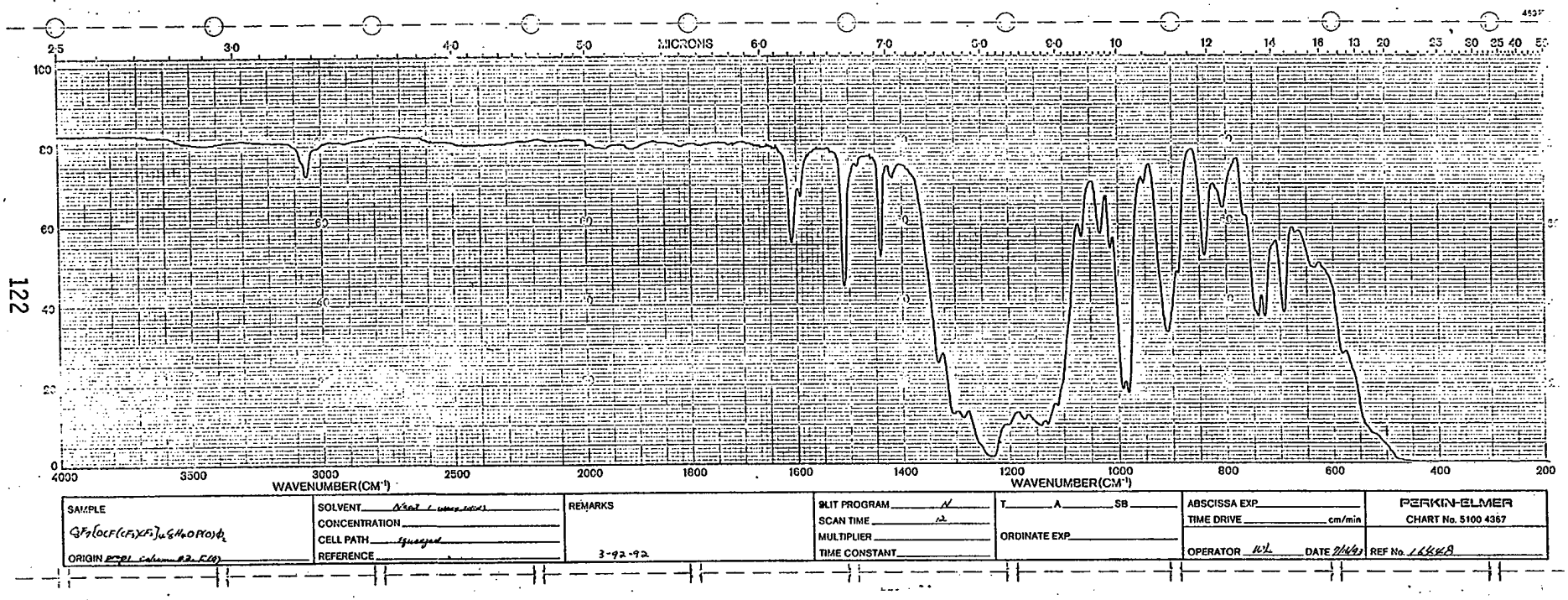


Figure 32. Infrared spectrum of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OP(O)(C_6H_5)_2$ (IX).

TABLE 34

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OP(O)(C_6H_5)_2$ (MW 1126)

m/e	%	m/e	%	m/e	%	m/e	%
31	8.4	125	3.0	170	2.5	342	2.3
47	12.9	126	3.2	171	6.9	343	14.0
50	9.8	127	3.9	172	10.2	344	4.5
51	11.2	128	2.9	173	3.4	443	4.8
66	2.5	131	3.3	183	4.3	675	7.2
69	42.2	141	2.1	199	6.8	676	2.3
75	2.4	142	4.1	200	4.0	841	9.4
76	2.2	143	8.9	201	100.0	842	3.2
77	25.3	145	5.9	202	23.9	1007	9.4
78	5.4	147	9.4	203	5.8	1008	2.9
95	3.9	150	9.9	214	2.1	1057	7.9
96	2.3	151	2.6	219	11.5	1059	2.5
97	5.2	152	4.8	220	5.1	1107	17.5
100	10.4	153	3.5	223	10.8	1108	6.3
107	2.1	154	4.2	224	2.2	1125	52.4
114	5.2	162	2.5	285	2.0	1126	66.5M^+
119	11.7	165	2.0	335	2.9	1127	26.0
123	2.1	169	24.9	341	3.9	1128	6.0

Peaks having intensities lower than 2% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e		m/e	
1126	M^+	201	$PO(C_6H_5)_2^+$
1107	$[M - F]^+$	169	$C_3F_7^+$
1057	$[M - CF_3]^+$	77	$C_6H_5^+$
1007	$[M - C_2F_5]^+$	69	CF_3^+
842	$[M - C_3F_7OCF(CF_3)]^+$		
675	$[M - C_3F_7OCF(CF_3)CF_2OCF(CF_3)]^+$		
343	$[M - C_3F_7[OCF(CF_3)CF_2]_3OCF(CF_3)]^+$		

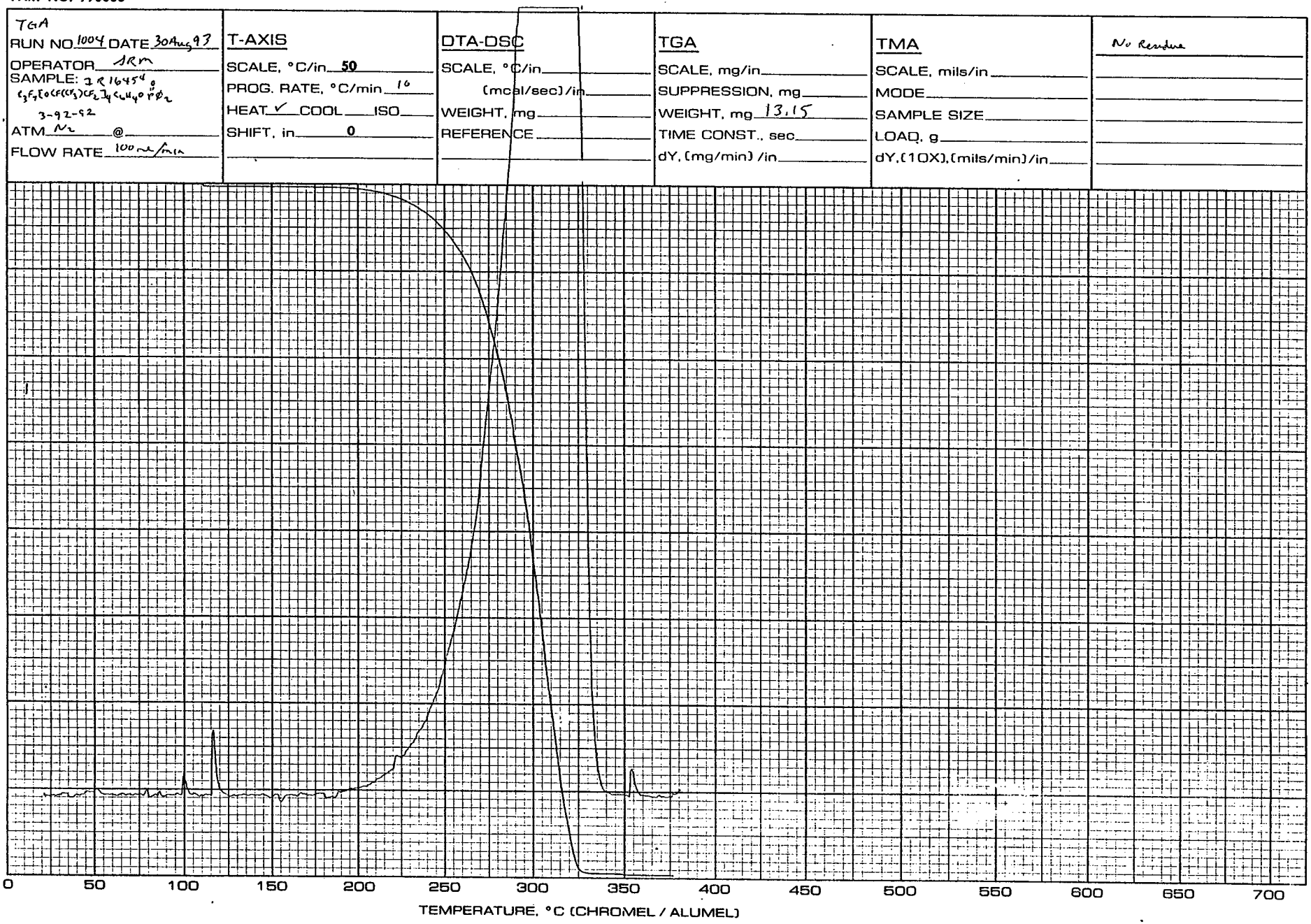


Figure 33. TGA of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OP(O)(C_6H_5)_2$ (IX) in N_2.

atmosphere enclosure and rinsed with Freon-113 (5 mL) and benzene (5 mL). The material (3.28 g) obtained on solvent evaporation in vacuo was mixed with 10% ether/hexanes (3.5 mL) and passed through a silica gel column (35 g, 26.5 cm x 2.2 cm, packed with 10% ether/hexanes). Elution with 10% ether/hexanes (250 mL) and 20% (300 mL) resulted in the recovery of 1.97 g of product which was freed from volatile impurities by heating at 80°C in vacuo to give 1.24 g (41% yield) of $\{C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O\}_2P(O)(C_6H_5)$ (GC purity 99%). The infrared spectrum is presented in Figure 34, the mass spectrum in Table 35 and the TGA trace in Figure 35.

Preparation of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OP(O)(OC_6H_5)_2$ (XI)

In an inert atmosphere enclosure into a stirred solution of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OH$ (3.00 g, 3.24 mmol) and $(C_6H_5O)_2P(O)Cl$ (0.87 g, 3.24 mmol) in benzene (5 mL) was added triethylamine (1.00 g, 9.69 mmol) in Freon-113 (5 mL) over a period of 0.5 h. Stirring at room temperature was continued for additional 0.5 h, then the reaction mixture was heated at 60°C under nitrogen bypass for 45 h. After cooling, the precipitated triethylamine hydrochloride was filtered off in an inert atmosphere enclosure and rinsed with Freon-113 (4 mL) and benzene (6 mL). Following solvent removal in vacuo, 3.77 g of light yellow liquid was obtained. The material was mixed with 10% ether/hexanes (5 mL) and passed through a silica gel column (40 g, 29 cm x 2.2 cm, packed in 10% ether/hexanes). Elution with 10% ether/hexanes (220 mL), and 20% ether/hexanes (200 mL) gave as the major fraction

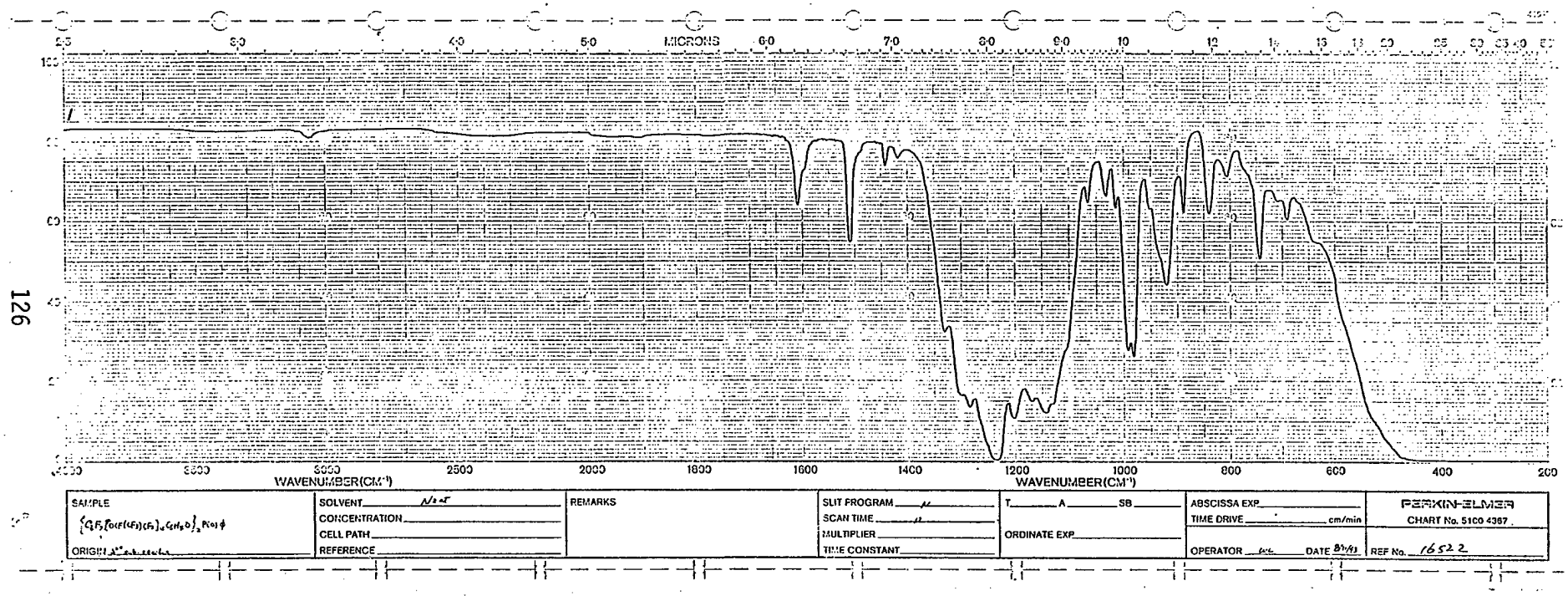


Figure 34. Infrared spectrum of $\{C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O\}_2P(O)(C_6H_5)$ (X).

TABLE 35

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
$\{C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O\}_2P(O)(C_6H_5)$ (MW 1974)

m/e	%	m/e	%	m/e	%	m/e	%
31	23.2	100	30.1	161	6.6	254	9.1
39	2.4	107	3.0	162	2.7	255	2.6
47	31.2	114	6.9	163	2.3	285	24.5
50	24.9	119	32.9	165	11.2	286	4.1
51	8.8	125	2.6	169	53.8	303	2.3
62	2.1	126	8.0	170	3.1	313	2.3
63	2.1	127	5.0	176	2.5	335	6.7
66	6.3	128	2.8	189	2.9	337	2.6
69	100.0	131	9.4	193	7.1	385	2.0
70	2.7	141	2.0	195	3.0	409	2.4
75	2.4	142	3.9	204	18.8	907	3.2
77	13.5	143	75.3	205	6.6	926	4.6
78	5.9	144	8.0	213	2.5	939	2.3
81	3.5	145	32.5	214	2.0	1049	2.6
88	2.5	146	2.7	219	2.3	1191	57.7
93	2.3	147	13.8	223	2.7	1192	10.7
95	4.0	150	24.7	243	10.8	1193	2.6
97	13.7	151	2.6	245	7.6		

Peaks having intensities lower than 2% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e		m/e	
1191	- $[M - C_3F_7[OCF(CF_3)CF_2]_3OCF(CF_3)]^+$	169	- $C_3F_7^+$
1049	- $[M - C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O]^+$	143	- $CF_2C_6H_4OH^+$, $FP(O)C_6H_5^+$
926	- $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OH^+$		
285	- $C_3F_7OCF(CF_3)^+$	119	- $C_2F_5^+$
243	- $CF(CF_3)CF_2C_6H_4OH^+$	69	- CF_3^+

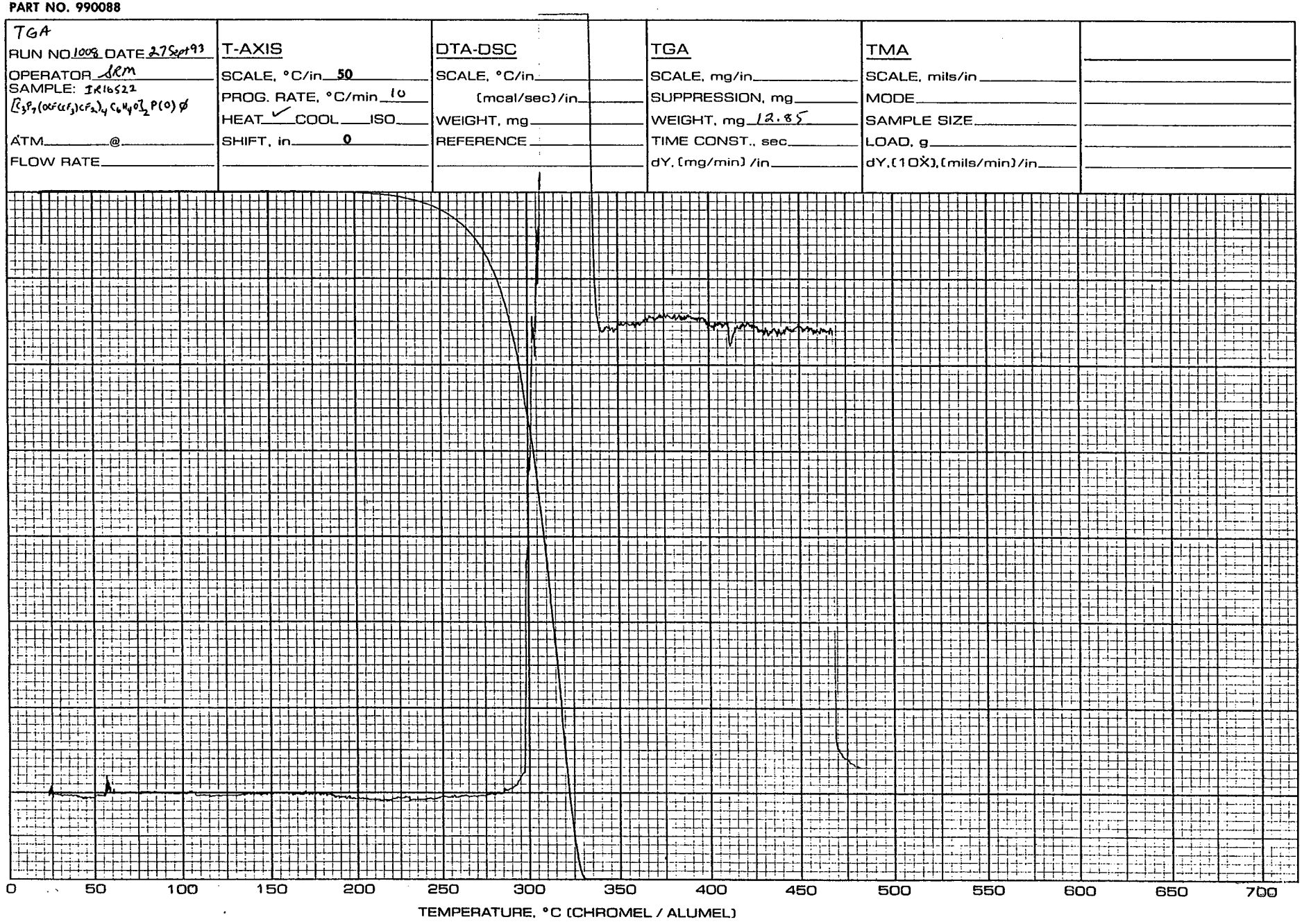


Figure 35. TGA of $\{C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O\}_2P(O)(C_6H_5)$ (X) in N_2.

3.08 g of clear colorless liquid (GC purity 97%). The last traces of impurities were removed by heating in vacuo at 75-80°C to give 2.79 g (74.4% yield) of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OP(O)(OC_6H_5)_2$ (GC purity 99.5%); MW,1100 (osmometry); theory, 1158. The infrared spectrum is given in Figure 36, the mass spectrum in Table 36 and the TGA trace in Figure 37.

Preparation of $\{C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O\}_2P(O)(OC_6H_5)$ (XIII)

In an inert atmosphere enclosure into a stirred solution of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OH$ (2.79 g, 3.01 mmol) and $C_6H_5OP(O)Cl_2$ (0.32 g, 1.52 mmol) in benzene (5 mL) was added triethylamine (1.53 g, 15.1 mmol) in Freon-113 (5 mL) over a period of 0.5 h. Stirring at room temperature was continued for additional 0.5 h, then the reaction mixture was heated at 65°C under nitrogen bypass for 45 h. After cooling, triethylamine hydrochloride was filtered off in an inert atmosphere enclosure and rinsed with Freon-113 (10 mL) and benzene (5 mL). The viscous liquid (3.02 g), obtained on evaporation of the solvents in vacuo, was mixed with 10% ether/hexanes (5 mL) and passed through a silica gel column (35g, 26 cm x 2.2 cm, packed in 10% ether/hexanes). Elution with 10% ether/hexanes (350 mL) resulted in 1.94 g of product. The last traces of impurities were removed by heating in vacuo at 75-80°C to give 1.15g (38.1% yield) of $\{C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O\}_2P(O)(OC_6H_5)$ (GC purity 99%); MW, 1980 (osmometry); theory, 1990. The infrared spectrum is given in

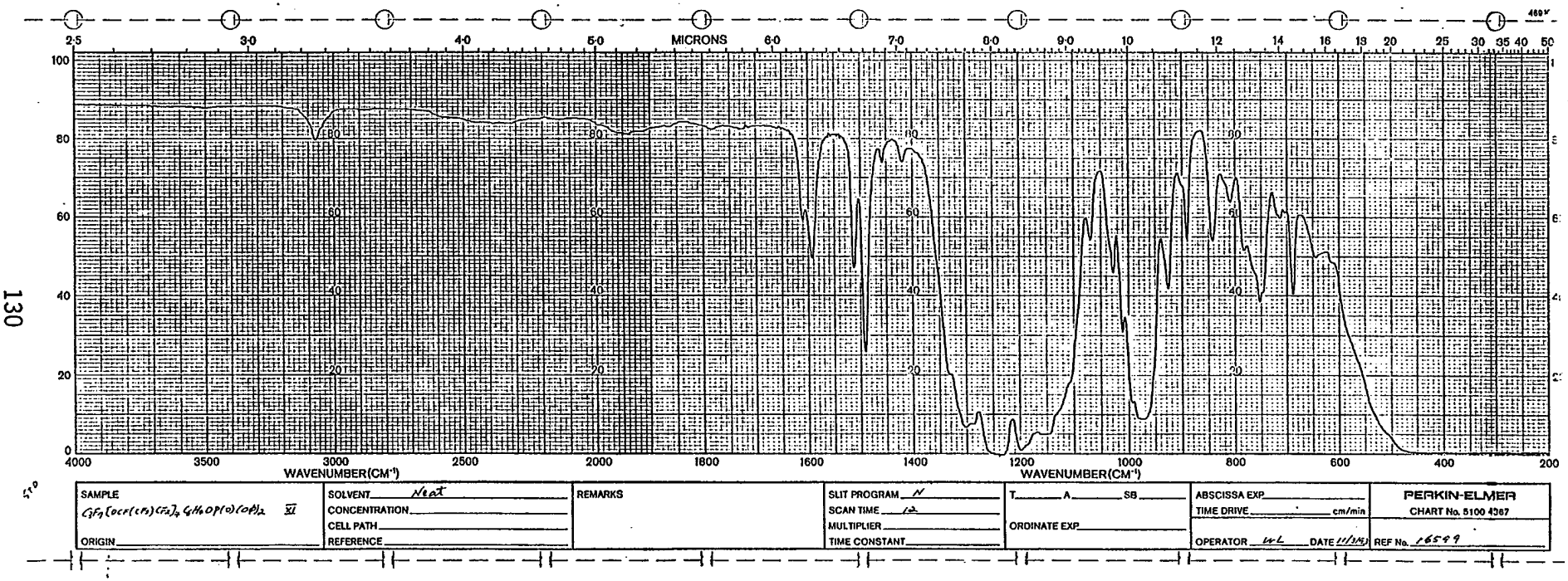


Figure 36. Infrared spectrum of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OP(O)(OC_6H_5)_2$ (XI).

TABLE 36

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OP(O)(OC_6H_5)_2$ (MW 1158)

m/e	%	m/e	%	m/e	%	m/e	%
31	17.3	100	25.3	188	43.0	373	4.0
36	3.5	112	4.2	189	13.0	375	100.0
38	5.1	114	6.7	191	3.7	376	32.9
39	18.5	119	29.1	203	7.7	377	8.7
47	23.6	126	7.9	205	9.5	393	6.9
50	22.0	127	7.5	213	6.6	425	3.3
51	17.5	128	4.4	215	18.5	435	3.5
62	3.2	131	9.0	216	4.1	475	9.5
63	7.3	139	8.2	217	7.1	476	3.8
64	5.1	140	14.7	218	4.6	541	6.6
65	27.7	141	7.9	219	16.5	641	5.9
66	12.7	142	5.8	220	4.5	707	14.2
67	3.1	143	23.4	223	3.4	708	4.8
69	73.1	144	3.4	227	3.0	873	15.8
70	3.6	145	10.4	232	5.3	874	6.7
75	5.5	147	14.7	233	16.1	973	3.7
76	6.8	150	18.6	234	3.9	1039	18.3
77	46.8	151	5.4	238	7.6	1040	6.5
78	12.6	152	6.8	251	3.0	1089	4.3
81	6.0	153	7.0	252	5.6	1139	12.8
92	4.4	154	4.2	255	3.0	1140	4.3
93	15.4	156	6.8	297	7.5	1157	16.7
94	15.6	168	8.2	299	3.7	1158	71.7M^+
95	4.9	169	47.8	301	7.8	1159	24.8
96	7.5	170	9.5	313	4.4	1160	6.0
97	12.3	187	4.5	335	6.0		

Peaks having intensities lower than 3% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e
1158 - M^+
1139 - $[M - F]^+$
1039 - $[M - C_2F_5]^+$
873 - $[M - C_3F_7OCF(CF_3)]^+$

m/e
375 - $CF_2C_6H_4OP(O)(OC_6H_5)_2^+$
233 - $P(O)(OC_6H_5)_2^+$
143 - $CF_2C_6H_4OH^+$

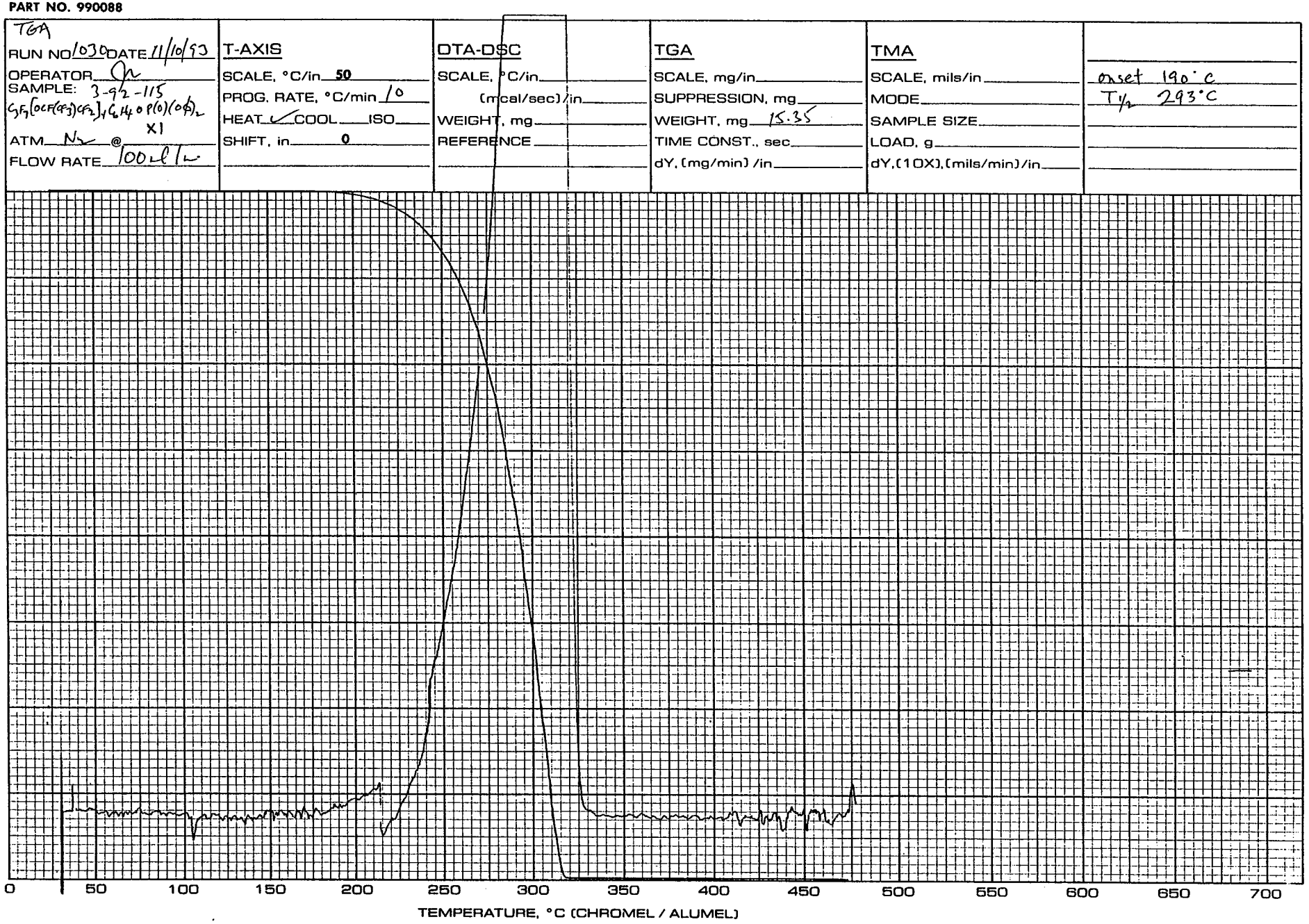


Figure 37. TGA of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OP(O)(OC_6H_5)_2$ (XI) in N_2.

Figure 38, the mass spectrum in Table 37, and the TGA trace in Figure 39.

Attempted preparation of n-$C_8F_{17}C_6H_4OH$ in DMSO

A mixture of 4-iodophenol (5.0 g, 22.7 mmol), copper bronze (4.7 g, 74.4 mmol), n-$C_8F_{17}I$ (13.6 g, 24.9 mmol) and DMSO (50 mL) was heated at 130°C under nitrogen bypass for 22 h. After cooling, it was added to a stirred solution of diethyl ether (150 mL) and water (150 mL). The bottom layer was extracted with additional diethyl ether (2 x 100 mL), washed with water (4 x 50 mL), and dried over anhydrous $MgSO_4$. Solvent removal in vacuo gave 10.2 g of yellow-brown semi-solid found to consist of two major components, n-$C_8F_{17}C_6H_4OH$ (A) (85%) and n-$C_7F_{15}C(O)C_6H_4OH$ (B) (9%) identified by their respective mass spectral breakdown patterns presented in Tables 38 and 39.

Typical Preparation of n-$C_8F_{17}C_6H_4OH$ in DMF

A mixture of 4-iodophenol (7.3 g, 32 mmol), copper bronze (7.0 g, 105 mmol) and n-$C_8F_{17}I$ (19.9 g, 35.0 mmol) in DMF (70 mL) was heated at 105°C under nitrogen bypass for 70 h. After cooling, the solution was decanted; the solid residue was mixed with diethyl ether (100 mL) and filtered. The filtrate was shaken with additional diethyl ether (100 mL) and water (200 mL). The top layer was separated and combined with the ether extract of the bottom layer, washed with water (4 x 50 mL) and dried over anhydrous $MgSO_4$. Removal of solvent in vacuo gave 16.3 g of

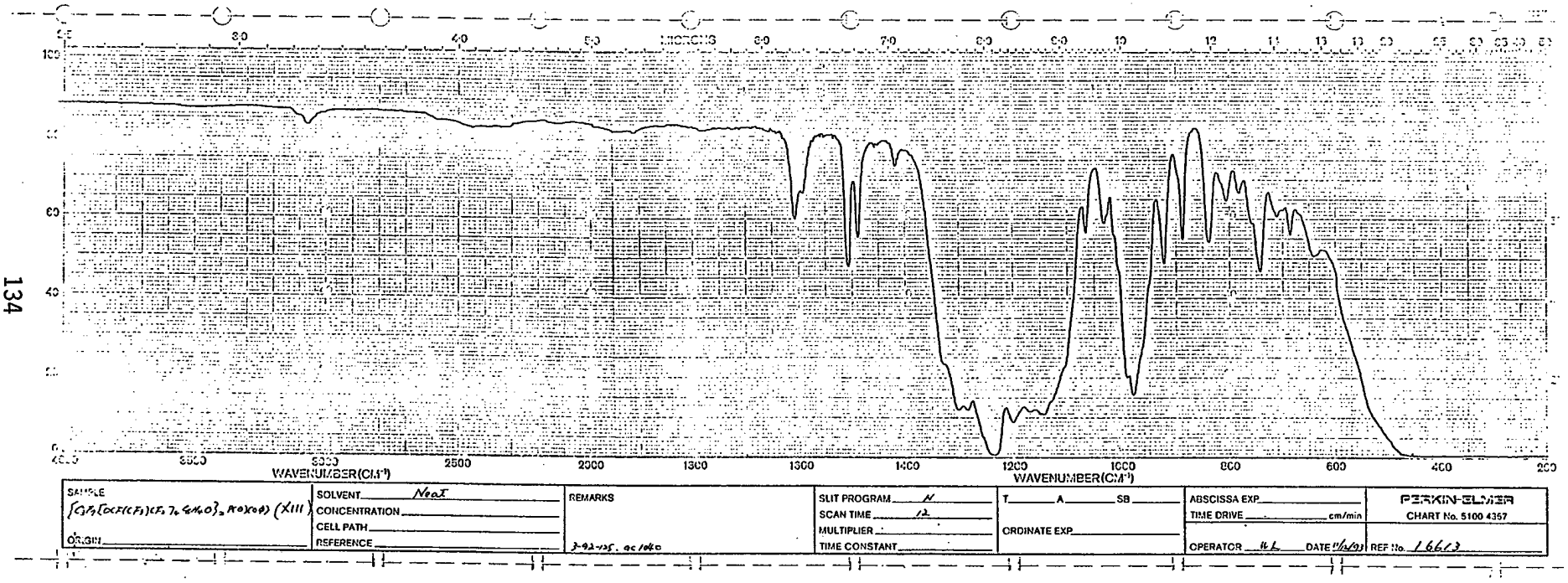


Figure 38. Infrared spectrum of $\{C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O\}_2P(O)(OC_6H_5)$ (XIII).

TABLE 37

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $\{C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O\}_2P(O)OC_6H_5$ (MW 1990)

m/e	%	m/e	%	m/e	%	m/e	%
31	28.7	88	3.2	144	5.3	213	13.3
36	7.1	93	7.0	145	32.2	219	7.5
38	4.7	94	8.9	146	5.4	221	4.1
39	8.0	95	4.6	147	19.7	223	7.7
47	32.1	96	7.3	150	33.4	225	3.7
50	31.8	97	20.6	151	6.3	227	9.6
51	8.7	100	34.2	161	7.5	237	3.4
62	3.6	101	3.0	163	4.4	243	5.1
63	5.1	107	7.7	169	70.9	245	10.4
65	10.0	112	3.3	170	5.5	262	13.2
66	13.8	114	8.3	176	3.6	263	6.7
67	3.1	119	37.2	181	7.3	285	3.1
69	100.0	125	3.5	189	12.1	301	17.0
70	4.2	126	11.3	193	3.6	302	3.4
75	6.8	127	11.2	195	6.0	313	4.6
76	4.4	128	4.2	201	3.7	335	11.1
77	25.6	131	13.2	203	5.1	345	6.7
78	11.6	140	5.2	205	6.9	926	3.2
81	6.2	142	5.0	211	4.2	1065	3.0
85	5.1	143	30.4	212	24.5	1207	99.5

Peaks having intensities lower than 3% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e

1207 - $[M - C_3F_7[OCF(CF_3)CF_2]_3OCF(CF_3)]^+$

1065 - $[M - C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O]^+$

301 - $CF_3C_6H_4OP(O)OC_6H_5^+$

212 - $CF_3CF_2C_6H_4OH^+$

143 - $CF_2C_6H_4OH^+$

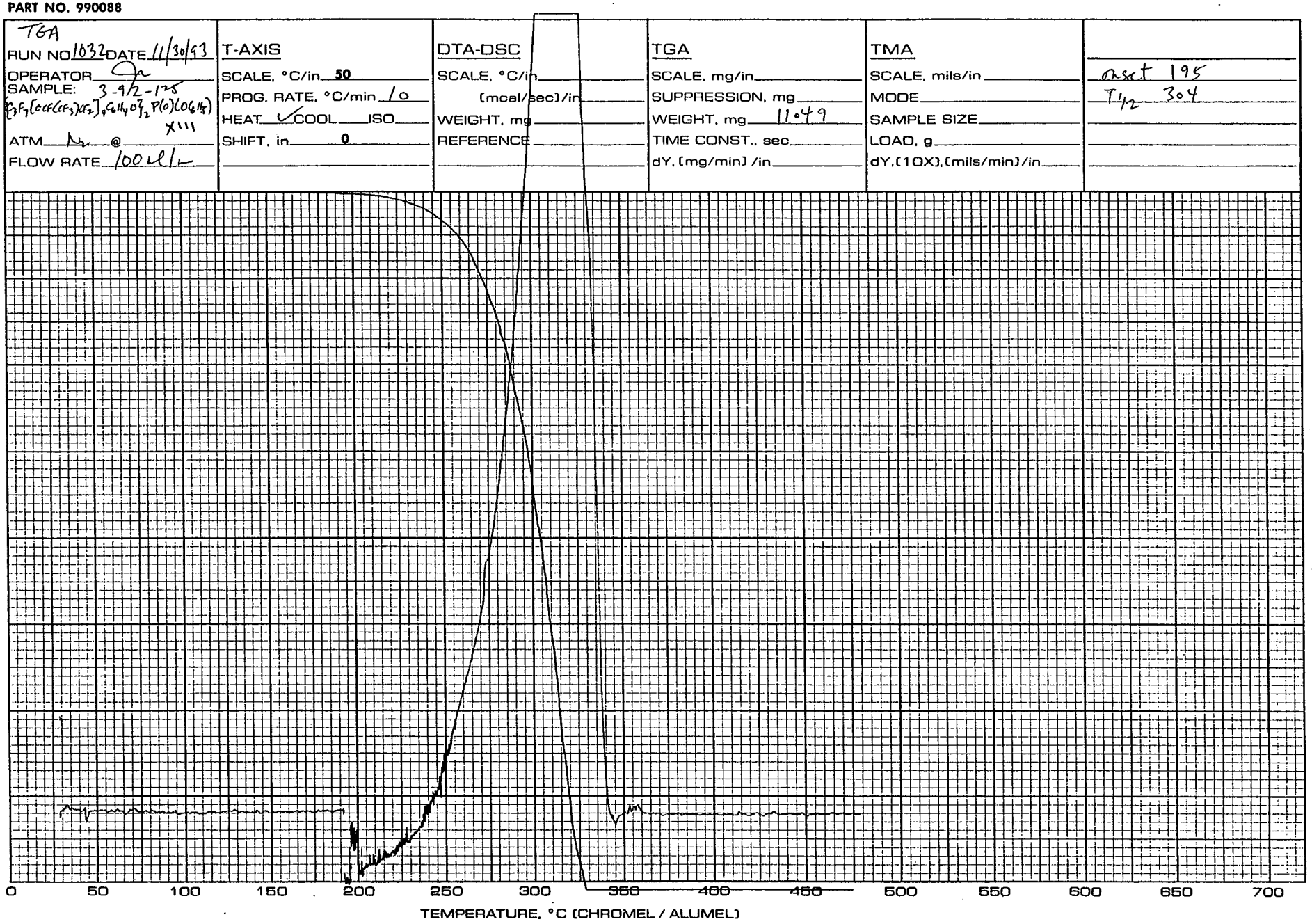


Figure 39. TGA of $\{C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O\}_2P(O)(OC_6H_5)$ (XIII) in N_2.

TABLE 38

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF n-$C_8F_{17}C_6H_4OH$ (MW 512)

m/e	%	m/e	%	m/e	%	m/e	%
31	5.4	93	3.1	142	5.0	176	8.1
36	1.7	94	2.0	143	100.0	181	1.7
38	2.0	95	12.3	144	16.6	192	1.9
39	5.1	96	1.5	145	49.4	194	1.5
50	6.0	99	2.1	146	5.8	204	2.1
51	3.6	100	9.0	150	1.5	443	2.0
53	1.6	113	2.0	156	1.7	464	5.5
57	1.9	114	10.4	157	1.7	473	9.7
63	3.5	115	1.8	161	4.1	492	29.6
65	3.4	119	11.2	163	1.7	493	17.2
69	23.0	121	6.1	169	2.2	494	2.6
75	6.6	123	1.6	172	2.4	511	1.6
81	4.5	125	6.9	173	81.5	512	20.2M^+
88	2.4	126	2.8	174	19.9	513	4.0
89	1.6	131	7.3	175	3.8		

Peaks having intensities lower than 1.5% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e

512 - M^+

493 - $[M - F]^+$

492 - $[M - HF]^+$

173 - $CF_2{=}CFC_6H_4O^+$

143 - $[M - C_7F_{15}]^+$

69 - CF_3^+

TABLE 39

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF n-$C_7F_{15}C(O)C_6H_4OH$ (MW 490)

m/e	%	m/e	%	m/e	%	m/e	%
31	2.7	64	6.4	94	2.5	149	5.7
37	1.0	65	28.4	100	6.8	169	1.2
38	4.2	66	3.8	114	1.7	174	2.0
39	16.0	69	11.1	119	4.9	220	1.2
50	2.6	71	1.2	120	6.8	443	2.7
51	1.4	75	1.4	121	100.0	471	13.2
53	3.4	76	1.0	122	17.0	472	2.5
60	1.1	81	1.8	123	2.9	490	11.9M^+
62	2.3	92	6.9	131	5.7	491	2.4
63	7.3	93	26.4	139	1.7		

Peaks lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e

490 - M^+

471 - $[M - F]^+$

121 - $[M - C_7F_{15}]^+$

93 - $C_6H_4OH^+$

69 - CF_3^+

yellow solid (GC purity 95%) which was sublimed at 65°C, resulting in 11.3 g of light yellow solid. Resublimation at 60°C gave 11.0 g (67.5% yield) of white solid n-$C_8F_{17}C_6H_4OH$, MP 74-75°C, (GC purity 99%). The infrared spectrum is presented in Figure 40.

Preparation of n-$C_8F_{17}C_6H_4OP(O)(C_6H_5)_2$ (XII)

In an inert atmosphere enclosure into a stirred solution of n-$C_8F_{17}C_6H_4OH$ (3.00 g, 5.86 mmol) and $(C_6H_5)_2P(O)Cl$ (1.38 g, 5.83 mmol) in benzene (10 mL) was added triethylamine (1.19 g, 11.8 mmol) in benzene (10 mL) over a period of 0.5 h. Stirring at room temperature was continued for an additional 0.5 h, then the reaction mixture was heated at 85°C under nitrogen bypass for 24 h. After cooling, the precipitated triethylamine hydrochloride was filtered in an inert atmosphere enclosure and rinsed with benzene (5 mL). From the filtrate solvents were removed <u>in vacuo</u> to give 4.15 g of a light yellow solid. Heating <u>in vacuo</u> at 65°C, followed by washing with 20% ether/hexanes (10 mL) afforded the product (3.38 g; GC purity 94%). The material was recrystallized from heptane/benzene to give 2.60 g (62.6% yield) of $C_8F_{17}C_6H_4OP(O)(C_6H_5)_2$, MP 110-111°C (GC purity 99%); MW, 740 (osmometry); theory, 712. The infrared spectrum is given in Figure 41; the mass spectrum in Table 40 and the TGA trace in Figure 42.

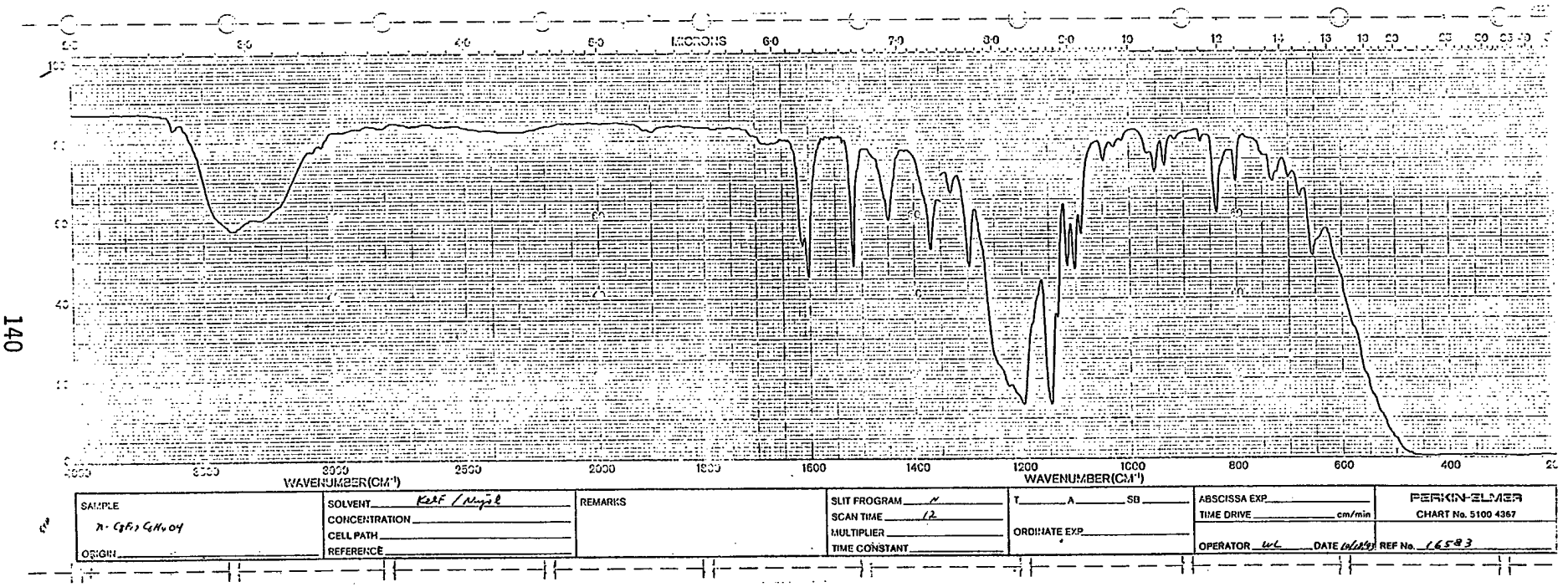


Figure 40. Infrared spectrum of $n\text{-}C_8F_{17}C_6H_4OH$.

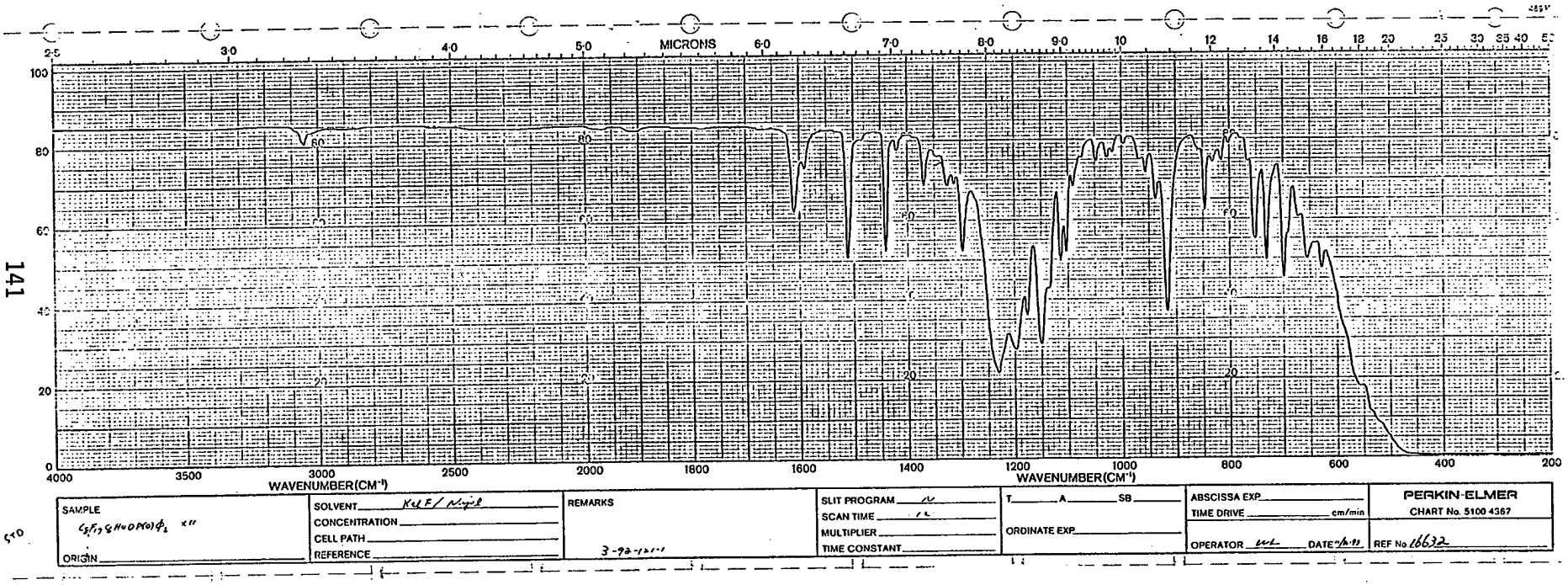


Figure 41. Infrared spectrum of n-$C_8F_{17}C_6H_4OP(O)(C_6H_5)_2$ (XII).

TABLE 40

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_8F_{17}C_6H_4OP(O)(C_6H_5)_2$ (MW 712)

m/e	%	m/e	%	m/e	%	m/e	%
31	2.8	119	3.3	162	2.1	220	7.7
32	3.0	125	2.5	169	2.3	223	4.3
47	3.2	126	2.1	171	4.6	341	2.7
50	5.2	127	3.5	172	4.0	342	2.0
51	10.5	131	4.7	173	5.6	693	5.9
69	11.9	142	4.9	176	2.3	709	4.2
75	2.4	143	13.7	183	4.8	711	30.2
77	19.8	144	2.0	199	7.3	712	32.8M^+
78	4.2	145	10.2	200	3.8	713	12.8
95	3.4	152	5.0	201	100.0	714	2.1
96	3.7	153	3.0	202	27.0		
100	4.1	154	4.2	203	4.3		
114	7.3	161	2.2	219	14.4		

Peaks having intensities lower than 2% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e

712 - M^+

693 - $[M - F]^+$

219 - $C_4F_9^+$

201 - $P(O)(C_6H_5)_2^+$

143 - $CF_2C_6H_4OH^+$

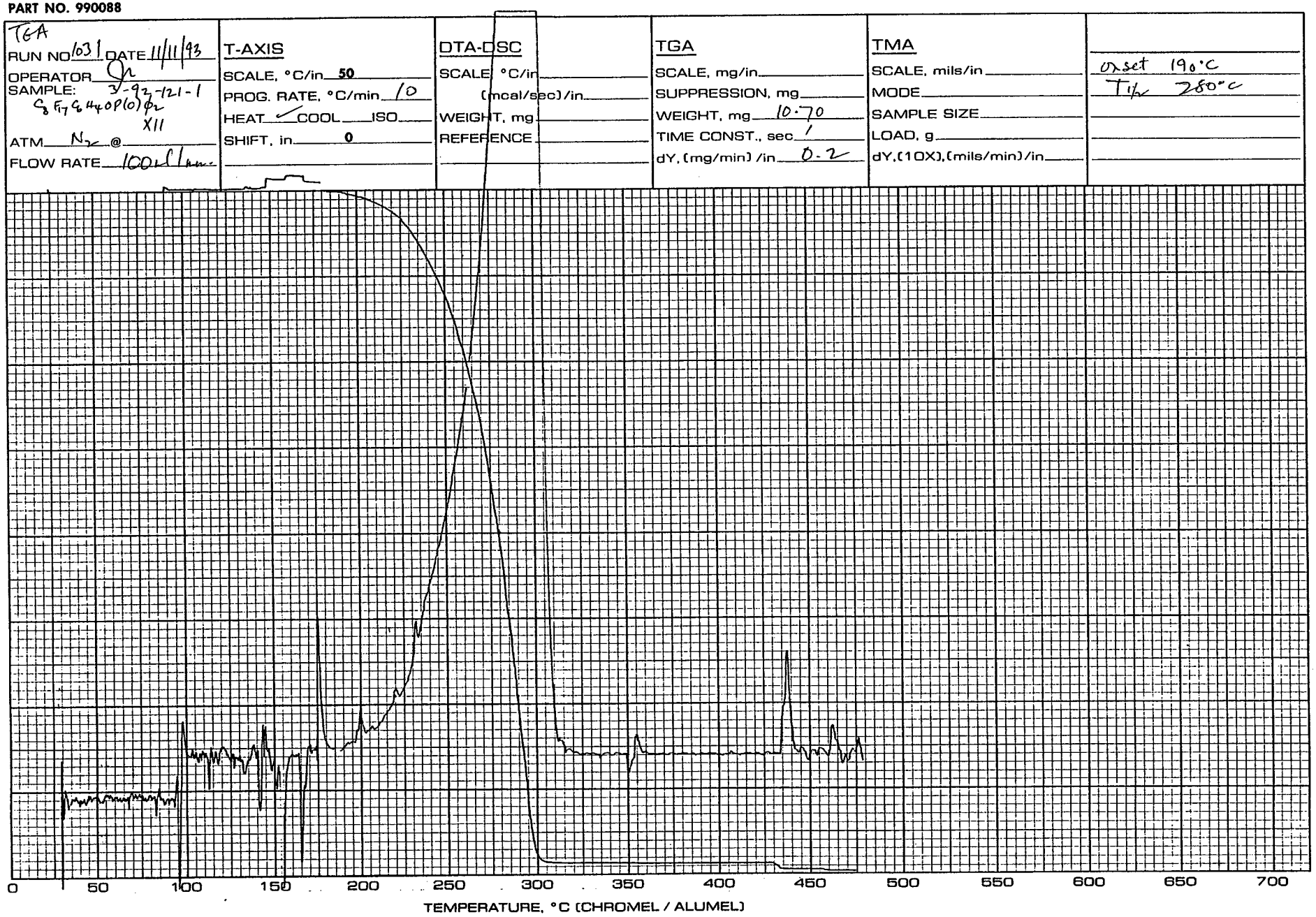


Figure 42. TGA of n-$C_8F_{17}C_6H_4OP(O)(C_6H_5)_2$ (XII) in N_2.

Preparation of $(n\text{-}C_8F_{17}C_6H_4O)_2P(O)(C_6H_5)$ (XIV)

In an inert atmosphere enclosure into a stirred solution of $n\text{-}C_8F_{17}C_6H_4OH$ (3.00 g, 5.86 mmol) and $(C_6H_5)P(O)Cl_2$ (0.57 g, 2.92 mmol) in benzene (6 mL)/Freon-113 (2 mL) was added triethylamine (1.2 g, 11.8 mmol) in Freon-113 (7 mL) over a period of 0.75 h. Stirring at room temperature was continued for an additional 0.5 h, then the solution was heated at 65°C under nitrogen bypass for 24 h. After cooling, the precipitated triethylamine hydrochloride was filtered off in an inert atmosphere enclosure and rinsed with benzene (5 mL) and Freon-113 (5 mL). The filtrate, after solvents removal, gave 3.31 g of a light yellow semi-solid (GC purity 80%); this was recrystallized from heptane/benzene, then from hexanes, to give 1.08 g (32% yield) of $(n\text{-}C_8F_{17}C_6H_4O)_2P(O)(C_6H_5)$, MP 84-85°C, (GC purity 95%). The infrared spectrum is given in Figure 43, the mass spectrum in Table 41 and the TGA trace in Figure 44.

Preparation of $n\text{-}C_8F_{17}C_6H_4OP(O)(OC_6H_5)_2$ (XV)

In an inert atmosphere enclosure into a stirred solution of $n\text{-}C_8F_{17}C_6H_4OH$ (3.00 g, 5.86 mmol) and $(C_6H_5O)_2P(O)Cl$ (1.57 g, 5.84 mmol) in benzene (5 mL) was added triethylamine (1.2 g, 11.8 mmol) in Freon-113 (5 mL) over a period of 40 minutes. Stirring at room temperature was continued for an additional 0.5 h, then the reaction mixture was heated at 65°C under nitrogen bypass for 24 h. After cooling, the precipitated triethylamine hydrochloride was filtered off in an inert atmosphere enclosure and rinsed with

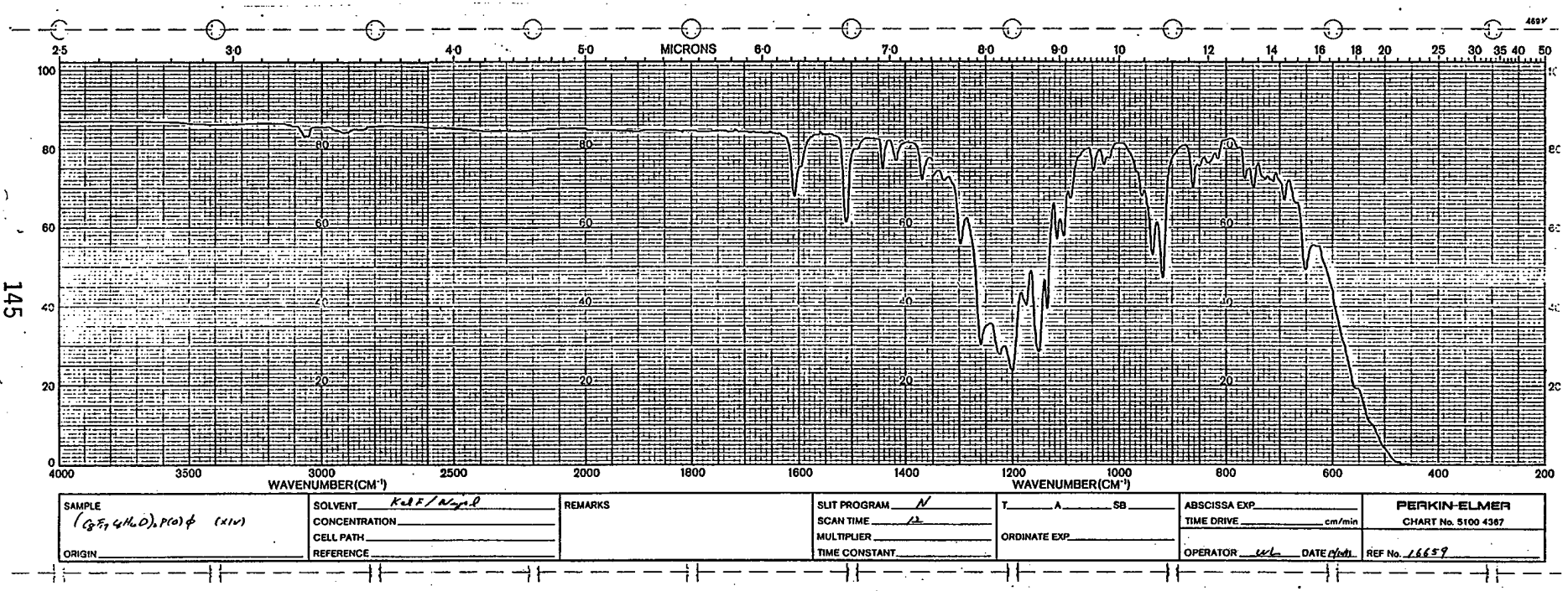


Figure 43. Infrared spectrum of $[n\text{-}C_8F_{17}C_6H_4O]_2P(O)(C_6H_5)$ (XIV).

TABLE 41

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $[n\text{-}C_8F_{17}C_6H_4O]_2P(O)C_6H_5$ (MW 1146)

m/e	%	m/e	%	m/e	%	m/e	%
31	8.5	131	15.7	204	100.0	634	11.1
47	9.9	141	9.2	205	41.3	635	62.3
50	9.8	142	9.4	206	3.0	636	21.6
51	16.1	143	32.2	207	4.6	637	18.8
63	3.2	144	6.1	213	9.1	638	4.2
69	35.8	145	40.4	214	3.7	653	3.7
75	4.8	146	6.1	217	4.0	654	5.1
76	5.3	157	3.7	219	20.5	711	4.2
77	49.8	161	7.5	220	15.2	712	3.9
78	5.9	162	4.3	226	5.2	777	79.3
81	4.1	163	3.1	229	5.4	778	31.4
95	5.4	165	3.4	250	3.1	779	8.6
96	4.8	169	7.0	265	10.5	795	5.5
100	12.6	173	6.0	266	3.9	1006	14.8
107	3.4	176	25.1	285	29.0	1007	5.0
113	3.0	177	3.4	286	5.3	1127	26.3
114	14.8	187	3.4	297	3.3	1128	10.0
119	16.2	189	20.7	379	10.1	1145	65.2
124	10.0	195	3.3	388	3.3	1146	92.2M^+
125	16.4	201	16.3	495	3.6	1147	31.0
126	25.8	202	4.8	588	18.2	1148	6.6
127	7.5	203	12.9	589	5.3		

Peaks having intensities lower than 3% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e		m/e	
1146	M^+	285	$CF_3C_6H_4OP(O)C_6H_5^+$
1127	$[M - F]^+$	204	$CF_2C_6H_3OP(O)_2^+$
777	$[M - C_7F_{15}]^+$	143	$CF_2C_6H_4OH^+$
635	$[M - C_8F_{17}C_6H_4O]^+$	77	$C_6H_5^+$

PART NO. 990088

TGA
RUN NO 1035 DATE 2/3/94
OPERATOR JA
SAMPLE: XIV
$[C_8F_{17}C_6H_4O]_2P(O)C_6H_5$
3-92-132
ATM N_2 @
FLOW RATE 100 cc/min

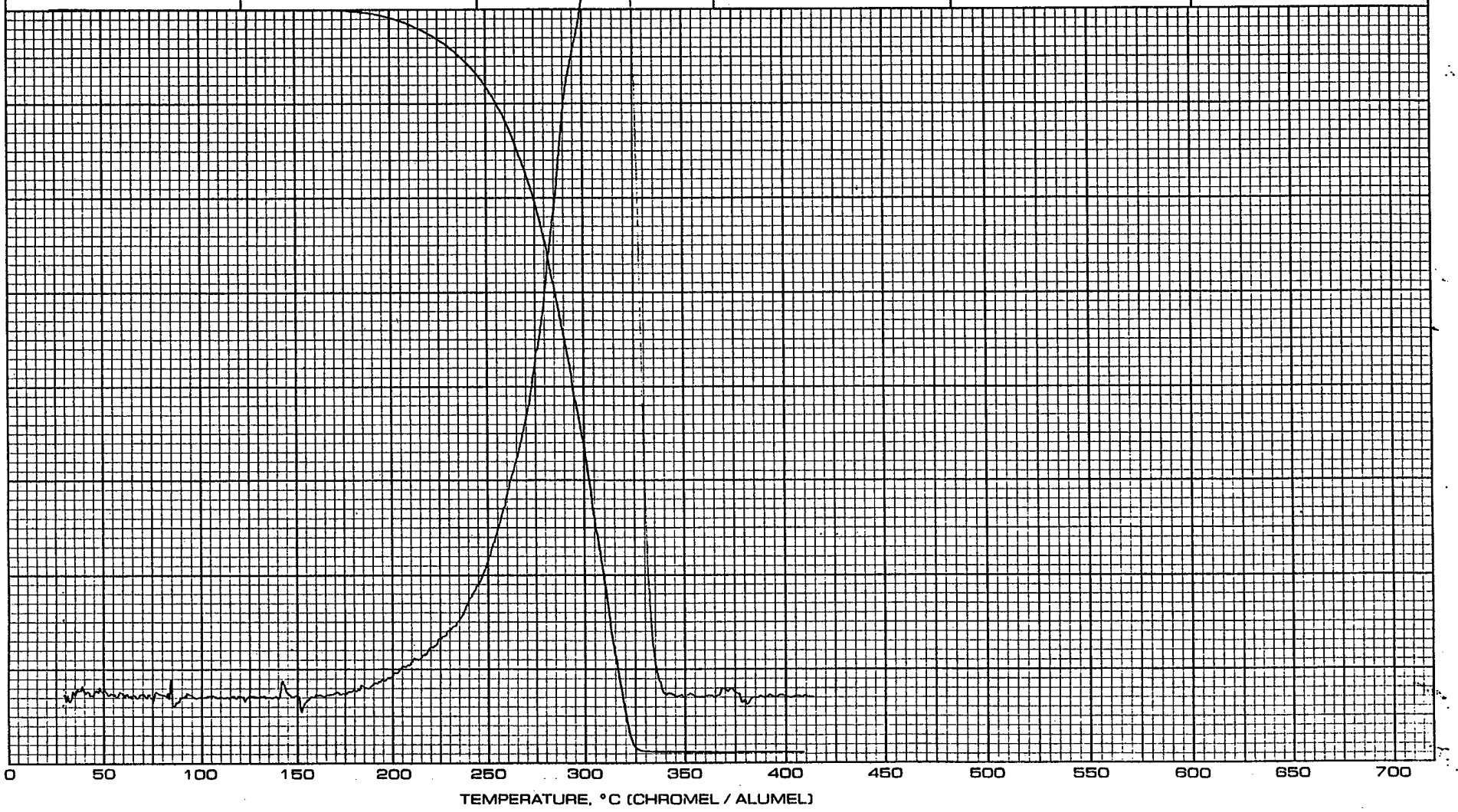
T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min 10
HEAT ✓ COOL ___ ISO ___
SHIFT, in 0

DTA-DSC
SCALE, °C/in ___
(mcal/sec)/in ___
WEIGHT, mg ___
REFERENCE ___

TGA
SCALE, mg/in 1
SUPPRESSION, mg 0
WEIGHT, mg 9.52
TIME CONST., sec 1
dY, (mg/min) /in 0.2

TMA
SCALE, mils/in ___
MODE ___
SAMPLE SIZE ___
LOAD, g ___
dY, (10X), (mils/min)/in ___

onset 180 °C
$T_{1/2}$ 294



MEASURED VARIABLE

DUPONT Instruments

147

Figure 44. TGA of $[n\text{-}C_8F_{17}C_6H_4O]_2P(O)(C_6H_5)$ (XIV) in N_2.

benzene (5 mL) and Freon-113 (5 mL). The filtrate, after solvent removal in vacuo at 70°C gave 4.37 g of a yellow semi-solid material (GC purity 80%). The powdery residue (4.0 g) was recrystallized twice from hexanes, to give 2.46 g (56.7% yield) of n-$C_8F_{17}C_6H_4OP(O)(OC_6H_5)_2$, MP 61-62°C, (GC purity >99%). The infrared spectrum is presented in Figure 45, the mass spectrum in Table 42 and the TGA trace in Figure 46.

Preparation of $C_3F_7[OCF(CF_3)CF_2]_2OCF(CF_3)C(O)C_6H_4Br$

Under nitrogen bypass, to 1,4-dibromobenzene (36 g, 0.153 mol) in diethyl ether (200 mL) at -5 to -10°C was added n-butyllithium (66 mL, 2.5M in hexanes, 0.165 mol) over a period of 1 h. After stirring for an additional 1.5 h, at -5 to -10°C, the solution was cooled to -78°C and the methyl ester, $C_3F_7[OCF(CF_3)CF_2]_2OCF(CF_3)CO_2CH_3$, (100 g, 0.148 mol), dissolved in ether (50 mL), was added over a period of 1.5 h. Stirring at -78°C was continued for another 1.5 h. Subsequently, hydrochloric acid (2N, 200 mL) was added and the mixture was stirred at room temperature overnight. The organic layer was separated, combined with the ethereal extract (75 mL) of the aqueous layer, washed with water (3 x 50 mL) and dried over anhydrous $MgSO_4$. Following solvent removal, distillation of the yellow liquid residue (113 g), gave 88.8 g (75% yield) of clear, colorless liquid $C_3F_7[OCF(CF_3)CF_2]_2OCF(CF_3)C(O)C_6H_4Br$, BP 70-77°C/ 0.001 mm Hg (GC purity >98%). The infrared and mass spectra are given in Figure 47, and Table 43, respectively.

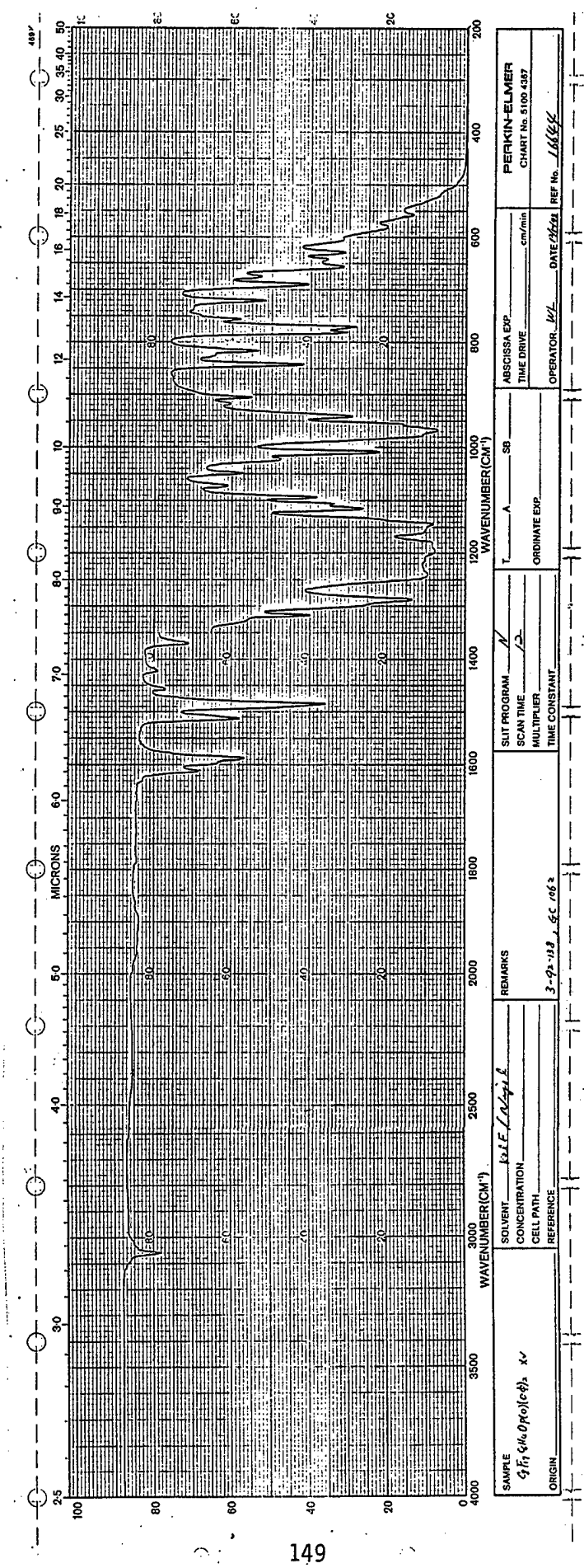


Figure 45. Infrared spectrum of n-$C_8F_{17}C_6H_4OP(O)(OC_6H_5)_2$ (XV).

TABLE 42

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $n\text{-}C_8F_{17}C_6H_4OP(O)(OC_6H_5)_2$ (MW 744)

m/e	%	m/e	%	m/e	%	m/e	%
31	3.4	94	17.7	156	5.9	232	4.7
39	21.3	100	4.5	168	10.5	233	16.4
47	10.3	114	8.5	169	9.2	277	6.3
50	6.8	119	3.9	170	8.4	281	8.2
51	21.8	126	6.1	176	3.1	375	81.4
63	7.9	127	3.5	187	3.2	376	32.1
93	14.1	153	3.4	188	47.7	377	4.2
64	4.1	131	3.9	189	10.0	651	4.7
65	29.6	139	6.9	205	19.9	667	3.0
66	4.3	140	15.3	215	20.7	725	23.5
69	12.8	141	6.3	216	3.6	726	9.0
75	4.0	142	5.9	217	6.1	743	56.5
76	4.1	143	23.9	218	4.7	744	100.0M^+
77	64.9	145	7.7	219	21.1	745	38.4
78	8.8	152	5.5	220	4.6	746	8.6

Peaks having intensities lower than 3% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e		m/e	
744	M^+	215	$C_6H_3OPOC_6H_5^+$
725	$[M - F]^+$	188	$CF_2C_6H_3OPO^+$
375	$[M - C_7F_{15}]^+$	143	$CF_2C_6H_4OH^+$

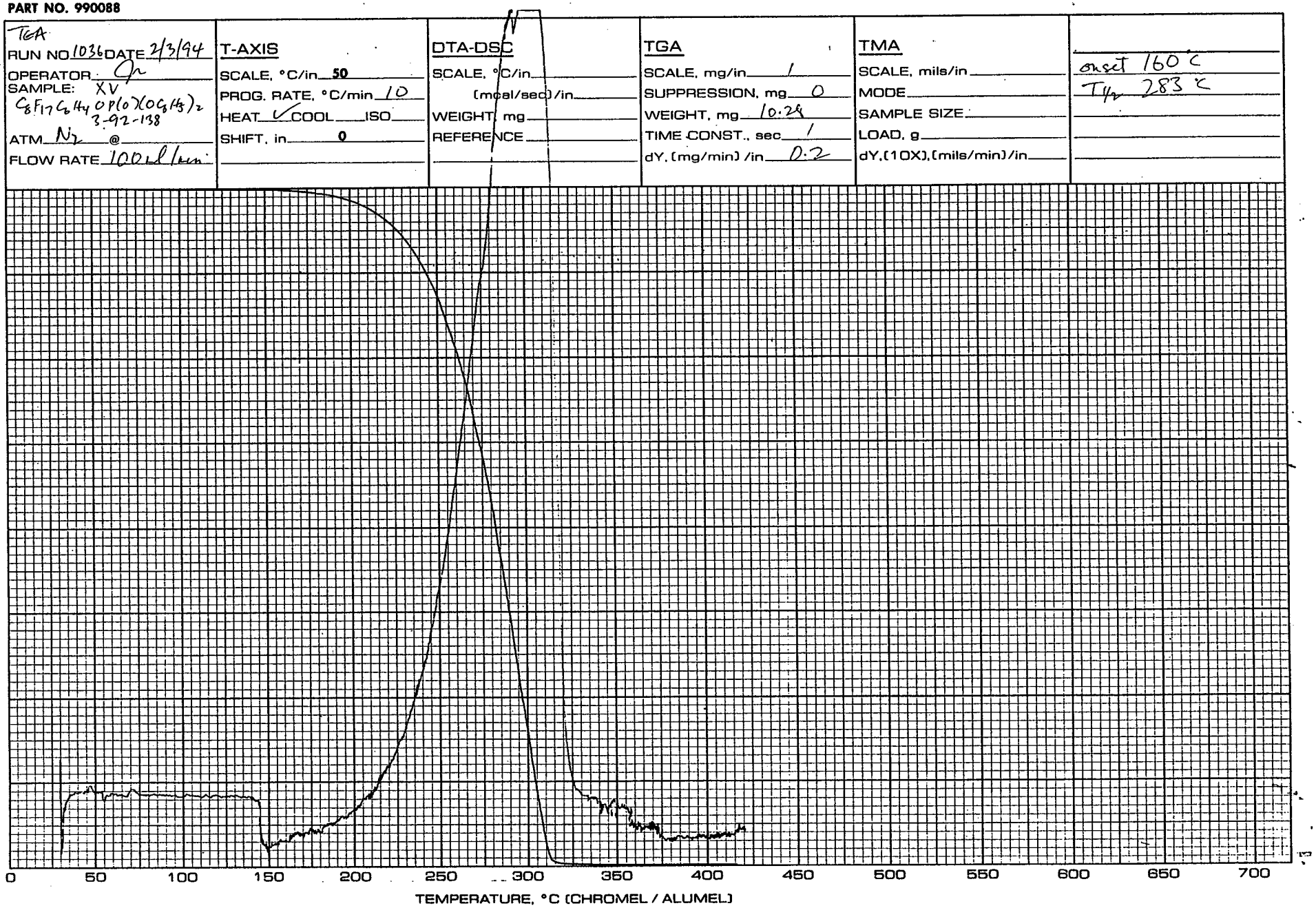


Figure 46. TGA of n-$C_8F_{17}C_6H_4OP(O)(OC_6H_5)_2$ (XV) in N_2

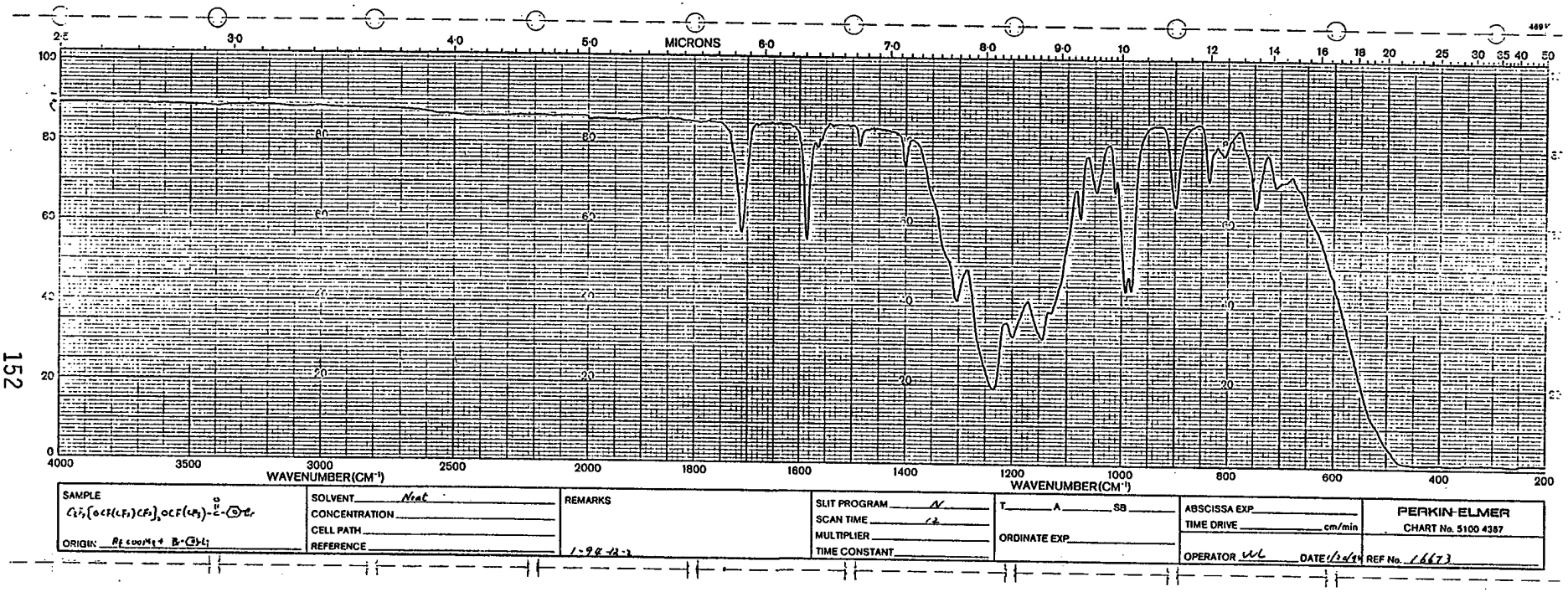


Figure 47. Infrared spectrum of $C_3F_7[OCF(CF_3)CF_2]_2OCF(CF_3)C(O)C_6H_4Br$.

TABLE 43

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7[OCF(CF_3)CF_2]_2OCF(CF_3)C(O)C_6H_4Br$ (MW 800)

m/e	%	m/e	%	m/e	%	m/e	%
31	4.9	104	12.7	184	14.4	351	3.1
47	4.1	105	7.0	185	100.0	449	10.1
50	15.8	119	8.7	186	16.7	451	9.4
51	4.0	131	3.3	204	3.8	615	3.5
69	31.1	147	5.5	205	4.9	617	3.1
74	6.2	150	8.4	207	4.6	731	2.0
75	20.6	155	28.2	255	10.1	781	4.6
76	27.6	156	4.7	257	10.4	783	4.5
77	5.0	157	27.2	283	3.5	800	$1.0M^+$
81	2.3	158	3.3	285	3.4	802	1.1
97	4.6	169	27.8	335	2.7		
100	9.6	183	98.2	349	3.2		

Peaks having intensities lower than 2% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e		m/e	
800	M^+	185	$C(O)C_6H_4{}^{81}Br^+$
781	$[M - F]^+$	183	$C(O)C_6H_4{}^{79}Br^+$
449	$[M - C_3F_7OCF(CF_3)CF_2O]^+$	157	$C_6H_4{}^{81}Br^+$
257	$CF(CF_3)C_6H_4{}^{81}Br^+$	155	$C_6H_4Br^+$
255	$CF(CF_3)C_6H_4{}^{79}Br^+$		

Preparation of $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4Br$

Into a Parr bomb (125 mL) containing Freon-113 (25 mL) and $C_3F_7[OCF(CF_3)CF_2]_2OCF(CF_3)C(O)C_6H_4Br$ (50.2 g, 62.7 mmol) cooled in Dry Ice was added, under nitrogen flow anhydrous hydrogen fluoride (~7 mL). Subsequently, sulfur tetrafluoride (19 g, 177 mmol) was condensed in. Following warming to room temperature, the bomb was agitated, using a shaker assembly, at 100-110°C (sand bath) for 22 h. After cooling to room temperature and venting the excess of SF_4 and gaseous products, Freon-113 (30 mL) was added and the mixture was poured onto ice-water (100 mL). Following washing with a saturated sodium bicarbonate solution (5 x 50 mL), water (3 x 50 mL), and drying over anhydrous $MgSO_4$ solvent was removed in vacuo to give 49.9 g of a viscous product. Two distillations resulted in 46.7 g (90.5% yield) of $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4Br$, BP 62-65°C/0.001 mm Hg (GC purity >99%). The infrared and mass spectra are given in Figure 48 and Table 44, respectively.

Preparation of $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OH$

Under nitrogen bypass, to diethyl ether (200 mL) and n-butyllithium (36 mL, 2.5 M in hexanes, 90.0 mmol) at -15°C was added $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4Br$ (57.5 g, 69.9 mmol) admixed with diethyl ether (15 mL), over a period of 1.25 h. After stirring for an additional 1 h at -15°C, the cold solution was added over an 1 h period (via a double-tip needle) to a solution of trimethyl

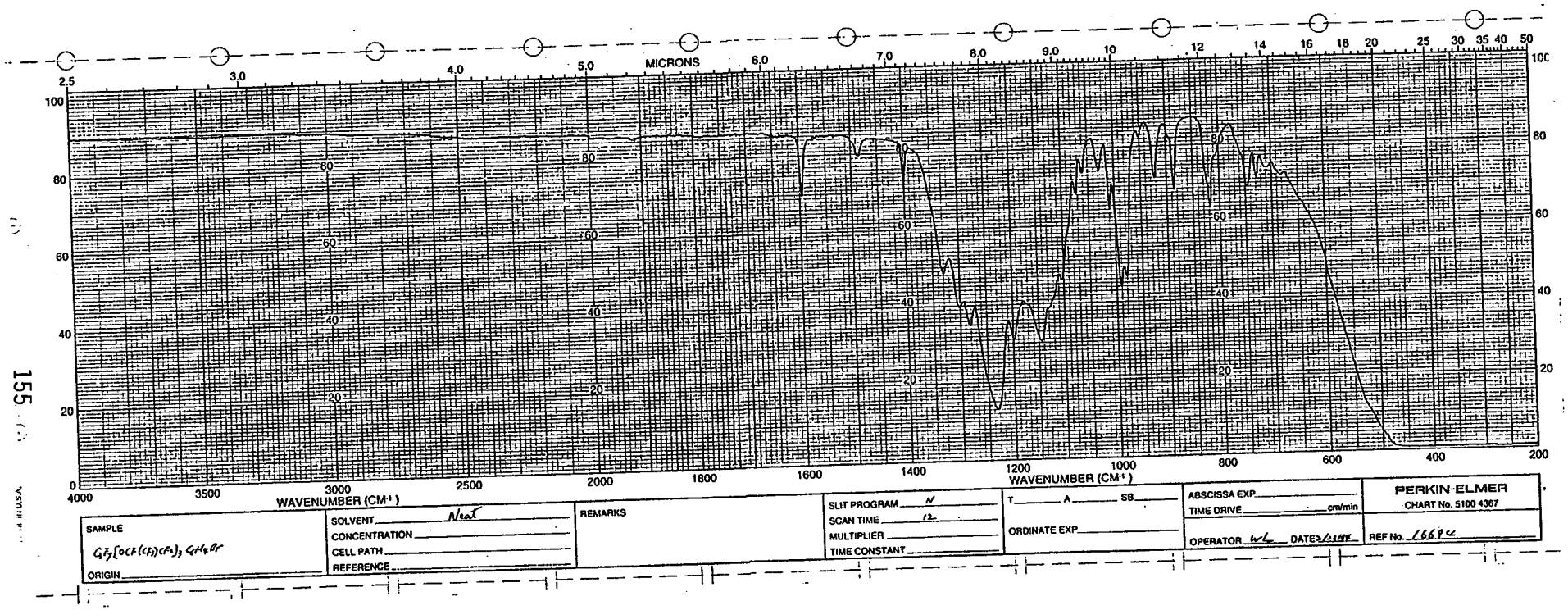


Figure 48. Infrared spectrum of $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4Br$.

TABLE 44

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4Br$ (MW 822)

m/e	%	m/e	%	m/e	%	m/e	%
31	4.6	127	8.6	225	3.7	308	4.0
47	3.9	131	2.5	226	7.1	335	4.0
50	9.0	145	6.3	236	2.4	471	7.8
51	2.3	147	6.1	238	2.0	473	8.4
69	42.0	150	6.1	245	3.9	703	2.8
74	2.0	157	4.1	255	11.7	705	2.8
75	7.7	169	39.4	257	12.3	803	4.5
76	5.9	170	2.2	285	4.8	805	3.5
81	2.5	176	3.8	287	4.3	822	21.2M+
100	11.0	195	5.9	302	2.1	823	6.1
107	4.1	205	100.0	304	2.8	824	18.2
119	10.2	206	15.9	305	26.0	825	5.2
125	9.9	207	88.5	306	5.2		
126	31.8	208	14.1	307	28.2		

Peaks having intensities lower than 2% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e		m/e	
822	M^+	305	$CF(CF_3)CF_2C_6H_4{}^{79}Br^+$
803	$[M - F]^+$	207	$CF_2C_6H_4{}^{81}Br^+$
471	$[M - C_3F_7OCF(CF_3)CF_2O]^+$	205	$CF_2C_6H_4{}^{79}Br^+$
307	$CF(CF_3)CF_2C_6H_4{}^{81}Br^+$	126	$CF_2C_6H_4^+$

borate (32.8 g, 316 mmol; distilled over sodium) in diethyl ether (200 mL) at -15°C. After 2 h stirring, acetic acid (20 g, 0.3 mol) was added and the solution was stirred for an additional 0.75 h. Hydrogen peroxide (30%, 47 mL in H_2O 47 mL) was then added at -15°C and the reaction mixture was stirred at room temperature overnight. Following addition of water (250 mL), the organic layer was washed with ferrous sulfate solution (30 g $FeSO_4.7H_2O$, 12 mL concentrated hydrochloric acid, 30 mL H_2O), water, and dried over anhydrous $MgSO_4$.

After solvent removal the crude product (51.7 g, 97.4% yield) was first purified by silica gel column chromatography (150 g, 3.0 cm x 44 cm, packed in 5% ether/hexanes). Elution using 5% ether/hexanes (535 mL), 10% (150 mL), 20% (50 mL) and 50% (400 mL) resulted in 4.4 g mainly of $C_3F_7[OCF(CF_3)CF_2]_3C_6H_5$ (the first yellow band) and 44.9 g (84.6% yield; GC purity 95%) of $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OH$ (the second yellow band). The latter portion was distilled to give 40.6 g (76.4% yield; GC purity >99%) of $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OH$, BP 73-77°C/0.001 mm Hg. The infrared and mass spectra are given in Figure 49 and Table 45, respectively. The preparations performed are summarized in Table 46.

Preparation of $[C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]_2P(O)OC_6H_5$ (XVI)

In an inert atmosphere enclosure into a stirred solution of $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OH$ (40.09 g, 52.73 mmol) and $C_6H_5OP(O)Cl_2$ (5.70 g, 27.02 mmol) in Freon-113 (140 mL) and benzene (25 mL) was

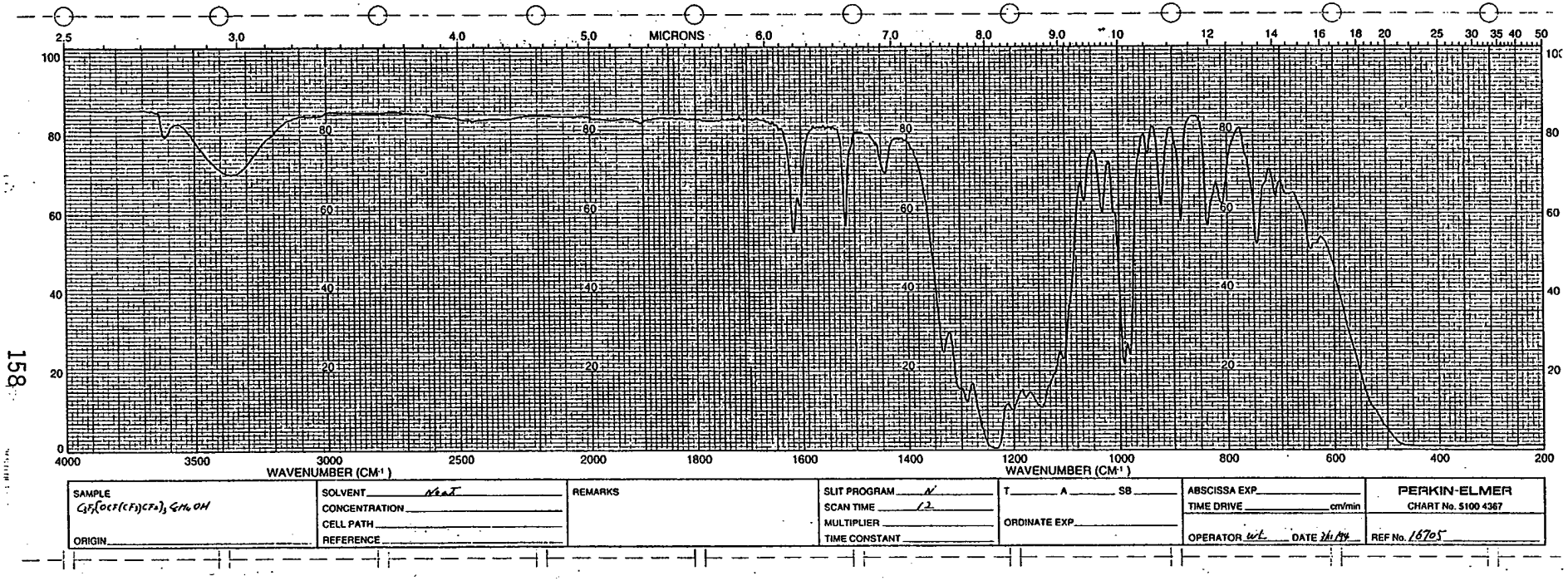


Figure 49. Infrared spectrum of $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OH$.

TABLE 45

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OH$ (MW 760)

m/e	%	m/e	%	m/e	%	m/e	%
31	7.2	100	14.2	161	5.5	309	5.9
39	7.2	113	3.1	169	33.0	335	4.5
47	5.4	114	10.8	170	3.4	339	6.1
50	6.9	115	3.9	171	4.1	389	3.1
51	4.3	119	11.4	174	6.9	409	12.9
63	5.4	131	4.8	193	22.6	475	5.4
65	7.1	141	3.5	194	5.2	621	5.0
69	43.9	142	7.9	214	3.3	641	8.3
75	4.9	143	100.0	220	4.0	691	3.7
88	4.5	144	26.4	223	8.1	741	13.1
89	3.3	145	8.8	224	4.6	742	4.0
95	9.7	147	7.1	243	30.2	760	25.4M^+
97	4.9	150	9.3	244	6.7	761	10.1

Peaks having intensities lower than 3% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e		m/e	
760	M^+	243	$CF(CF_3)CF_2C_6H_4OH^+$
741	$[M - F]^+$	193	$C_2F_4C_6H_4OH^+$
409	$[M - C_3F_7OCF(CF_3)CF_2O]^+$	143	$CF_2C_6H_4OH^+$

TABLE 46

SUMMARY OF PREPARATIONS OF $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OH$[a]

	STEP 1						STEP 2				STEP 3			STEP 4		
	$R_fC_6H_4Br$[b]		n-BuLi		Et_2O	Time[e]	$B(OMe)_3$		Et_2O	Time[e]	HOAc		Time[e]	H_2O_2/H_2O[f]	Product	
Entry	g	mmol	mL	mmol	mL	min	g	mmol	mL	min	g	mmol	min	mL/mL	g	yield%
1	23.4	28.4	16	40.0	20[c] 125[d]	75	15.3	147	150	120	8.0	133	60	19/19	13.8	64.2
2	21.9	26.6	14	35.0	20[c] 125[d]	80	13.6	131	150	180	7.9	132	60	19/19	12.3	60.9
3	40.2	48.8	25	62.5	20[c] 125[d]	90	28.0	269	150	120	16.4	273	60	36/36	26.1	70.4
4	61.2	74.3	38	95.0	15[c] 225[d]	50	35.5	342	225	120	20.7	345	45	51/51	44.0	76.9
5	55.6	67.6	35	87.5	15[c] 200[d]	60	32.7	315	200	120	19.3	322	35	47/47	39.2	76.3

a) The process comprised four steps performed at -15 to -20°C; $R_fC_6H_4Br/Et_2O$ was added to n-BuLi/Et_2O; the resultant solution (cold) was added to $B(OMe)_3/Et_2O$ (via a double-tip needle) followed by treatments with HOAc and H_2O_2/H_2O.
b) $R_f = C_3F_7[OCF(CF_3)CF_2]_3$.
c) Diethyl ether mixed with $R_fC_6H_4Br$.
d) Diethyl ether mixed with n-BuLi.
e) The solution was stirred for the denoted period after addition of reagent.
f) H_2O_2, 30% concentration. The reaction mixture was stirred at low temperature for 45 minutes, then at room temperature overnight.

added triethylamine (10.7 g, 0.105 mol) in benzene (35 mL) over a period of 1.5 h. Stirring at room temperature was continued for an additional 0.5 h, then the reaction mixture was heated at 65°C under nitrogen bypass for 44 h. After cooling, the precipitated triethylamine hydrochloride (7.4 g) was filtered off and rinsed with Freon-113. The product (44.0 g), obtained after solvent removal in vacuo, was purified by a silica gel chromatography (200 g, 53 cm x 3 cm, packed in 10% diethyl ether/hexanes). Elution was done with 10% (360 mL), 20% (200 mL), 25% (100 mL), and 30% (600 mL) of diethyl ether/hexanes. No phosphate was present in the first 660 mL; the next 650 mL gave clear, colorless liquid (37.7 g), which was further purified by subliming out the remaining impurities at 85-90°C. This resulted in 35.8 g (82% yield) of $\{C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O\}_2P(O)OC_6H_5$ (GC purity > 99%). The infrared spectrum is given in Figure 50, the TGA trace in Figure 51 and the mass spectrum in Table 47.

Preparation of $[C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]_2P(O)C_6H_5$ (XVII)

In an inert atmosphere enclosure into a stirred solution of $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OH$ (3.90 g, 5.13 mmol) and $C_6H_5P(O)Cl_2$ (0.50 g, 2.56 mmol) in Freon-113 (10 mL) was added triethylamine (1.60 g, 15.8 mmol) in benzene (5 mL) over a period of 0.5 h. Following stirring for an additional 0.5 h at room temperature, the reaction mixture was heated at 65°C under nitrogen bypass for 24 h. After cooling, the precipitated triethylamine hydrochloride was filtered off and the material (3.47 g), obtained on

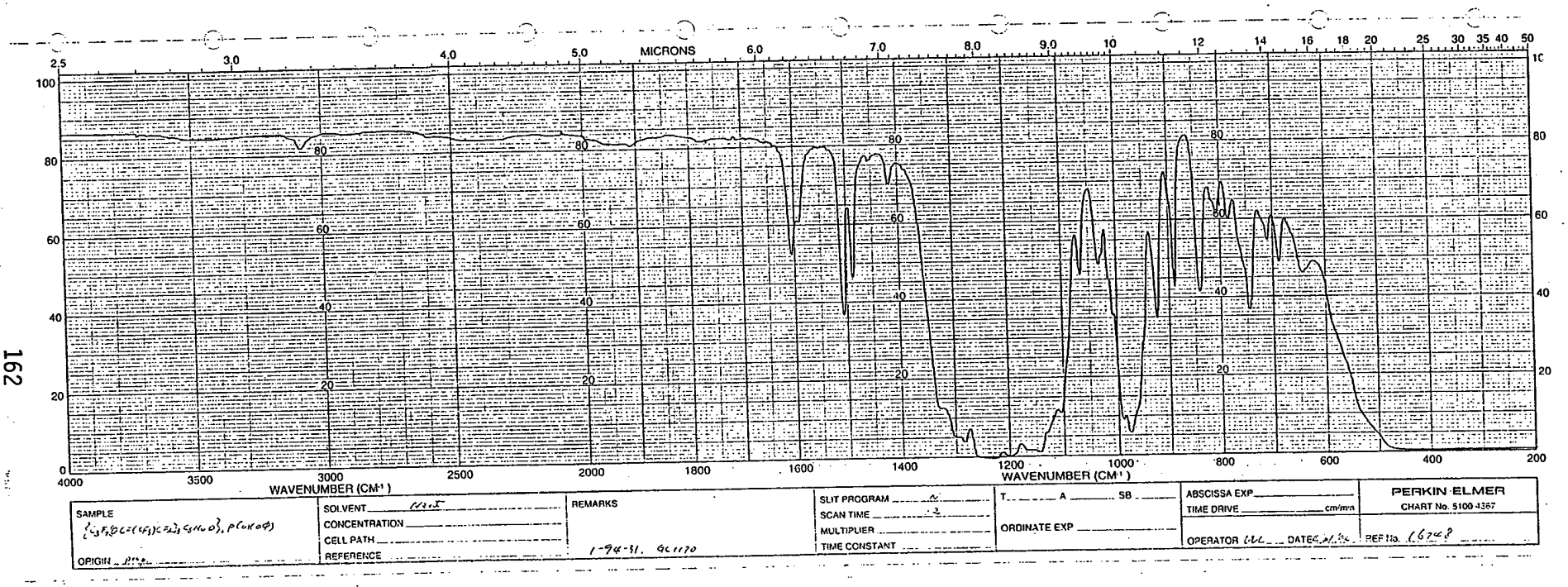


Figure 50. Infrared spectrum of $\{C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O\}_2P(O)OC_6H_5$ (XVI).

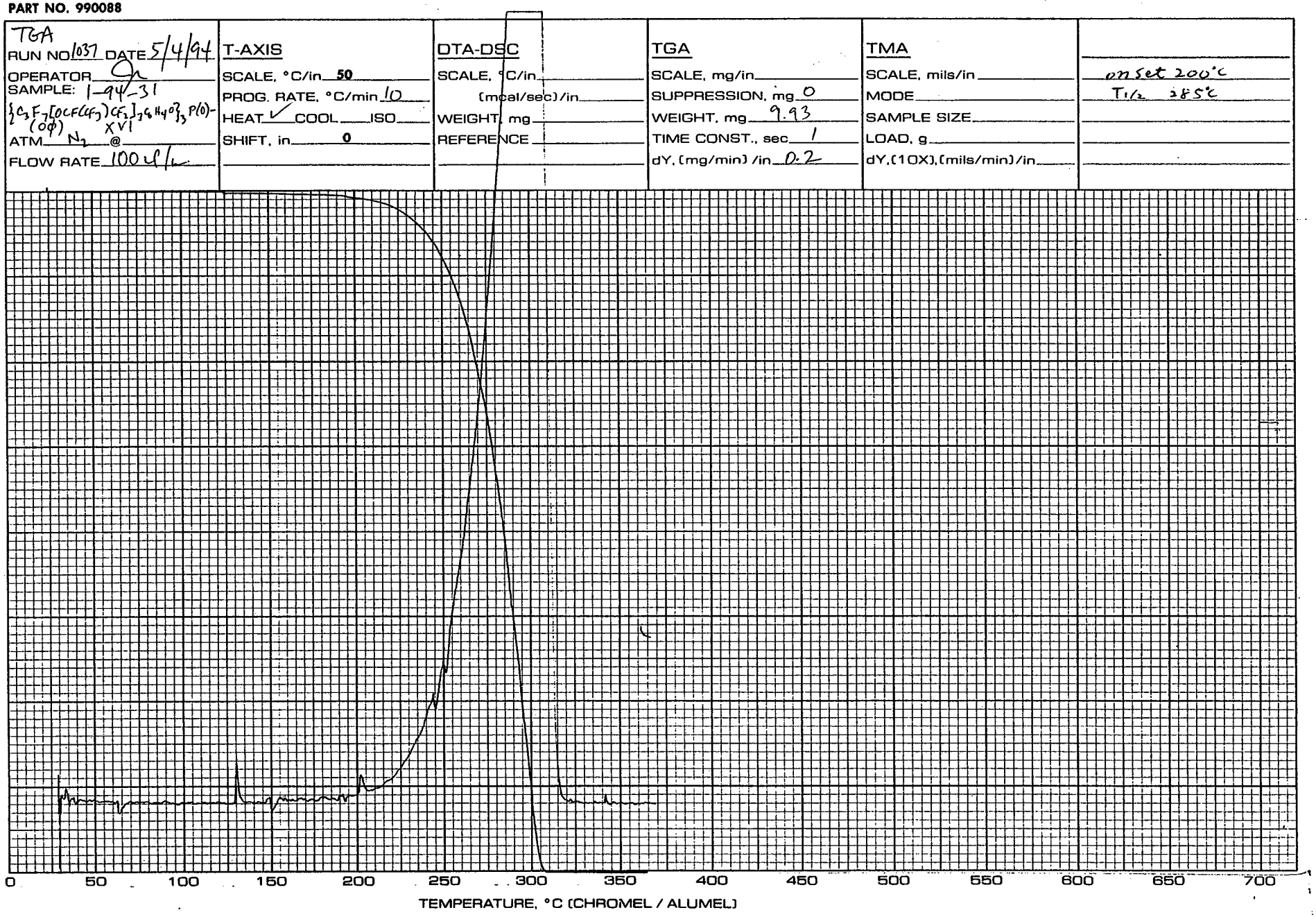


Figure 51. TGA of $\{C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O\}_2P(O)OC_6H_5$ (XVI) in N_2.

TABLE 47

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $\{C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O\}_2P(O)OC_6H_5$ (MW 1658)

m/e	%	m/e	%	m/e	%	m/e	%	m/e	%
31	35.3	92	9.0	143	83.4	213	19.5	477	12.8
37	5.6	93	24.6	144	17.8	214	78.3	621	22.3
38	13.4	94	35.2	145	80.3	215	15.1	622	7.6
39	27.8	95	23.0	146	14.9	217	7.1	633	9.8
40	7.3	96	7.6	147	49.2	219	16.3	643	9.0
47	29.6	97	38.1	150	43.3	220	10.0	671	17.5
49	6.6	98	7.5	151	36.2	221	9.7	712	17.7
50	33.7	99	10.0	155	6.3	223	82.3	721	22.9
51	24.4	100	57.3	156	8.0	224	28.2	722	8.6
53	9.5	101	5.7	157	7.4	225	17.6	738	7.0
55	6.7	104	7.5	161	13.0	227	38.5	740	77.1
57	8.4	105	6.0	163	13.6	228	8.1	741	30.5
62	10.6	107	13.0	164	16.4	239	9.9	742	10.3
63	22.3	111	7.6	169	87.8	242	23.2	760	17.5
64	11.4	112	6.5	170	21.6	243	19.7	799	8.4
65	28.2	113	9.8	171	7.6	245	14.4	809	7.3
66	28.4	114	28.7	173	18.8	262	13.5	899	18.7
67	6.3	115	6.9	174	12.0	273	11.9	900	7.0
68	7.0	119	67.1	175	20.5	285	7.4	909	12.0
69	100.0	120	10.5	176	16.0	301	74.4	918	51.1
70	12.3	121	77.2	178	22.2	302	25.0	919	25.6
73	14.0	122	16.0	183	7.1	311	10.3	920	8.5
74	10.0	123	16.4	189	14.9	313	13.2	963	5.3
75	26.9	125	21.2	191	12.1	327	9.2	967	17.9
76	18.9	126	18.8	192	22.9	335	21.8	968	8.0
77	32.4	127	14.0	193	22.1	351	7.2	1041	62.8
78	13.9	128	6.9	194	9.8	361	12.1	1042	36.7
81	15.1	131	18.3	195	30.7	387	9.4	1043	12.5
83	6.4	139	5.8	205	15.0	389	11.6	1059	10.0
85	9.1	140	8.1	207	6.5	401	11.2		
87	8.4	141	12.4	211	13.7	409	8.4		
88	12.1	142	23.9	212	22.8	411	7.0		

Peaks having intensities lower than 5% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e

1041 - $[M - C_3F_7[OCF(CF_3)CF_2]_2OCF(CF_3)]^+$

918 - $[C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OPF(O)OC_6H_5]^+$

899 - $[M - C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]^+$

740 - $[M - C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OPF(O)OC_6H_5]^+$

301 - $[CF_3C_6H_4OP(O)OC_6H_5]^+$

223 - $[CF_3CF{=}CFC_6H_4O]^+$

143 - $[CF_2C_6H_4OH]^+$

evaporation of the filtrate, was mixed with 10% diethyl ether/hexanes (3 mL) and passed through a silica gel column (40 g, 29 cm x 2.2 cm, packed in 10% diethyl ether/hexanes). Elution using 10% and 20% diethyl ether/hexanes, 325 and 250 mL respectively, resulted in 2.81 g of product. The remaining impurities were sublimed out at 70-90°C to give 2.26 g (53% yield) of a clear, colorless liquid $[C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]_2P(O)C_6H_5$ (GC purity 99%). The infrared spectrum is given in Figure 52, the TGA trace in Figure 53 and the mass spectrum in Table 48.

Preparation of $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_{2-x}P(O)OC_6H_5(OH)_x$ (VII-AS)

a) By reaction of $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OH$ with an excess of $C_6H_5OP(O)Cl_2$

In an inert atmosphere enclosure into a stirred solution of $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OH$ (2.51 g, 4.21 mmol) and $C_6H_5OP(O)Cl_2$ (0.59 g, 2.8 mmol) in Freon-113 (10 mL) was added triethylamine (0.85 g, 8.4 mmol) in benzene (5 mL) over a period of 0.25 h. After stirring for an additional 0.5 h at room temperature, the reaction mixture was heated at 65°C under nitrogen bypass for 22 h. Following cooling to room temperature, the precipitated triethylamine hydrochloride was filtered off and the filtrate after evaporation <u>in vacuo</u>, gave 2.92 g of light yellow liquid. Distillation resulted in 1.86 g of product, BP 140-170°C/0.001 mm Hg. Quantitative GC analysis showed it to contain 66% of $[C_3F_7[OCF(CF_3)CF_2]_2]_2C_6H_4O]P(O)OC_6H_5$. The TGA is presented in Figure 54; the material provided total rust protection under CREP

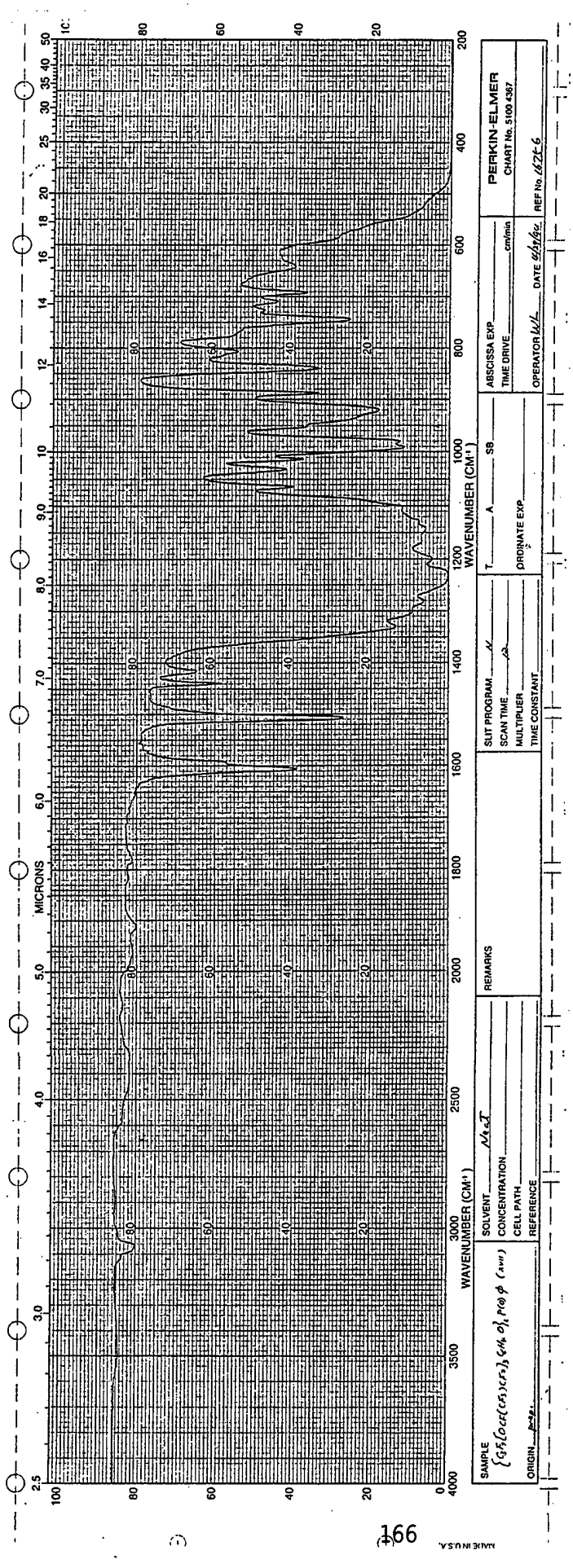


Figure 52. Infrared spectrum of $\{C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O\}_2P(O)C_6H_5$ (XVII).

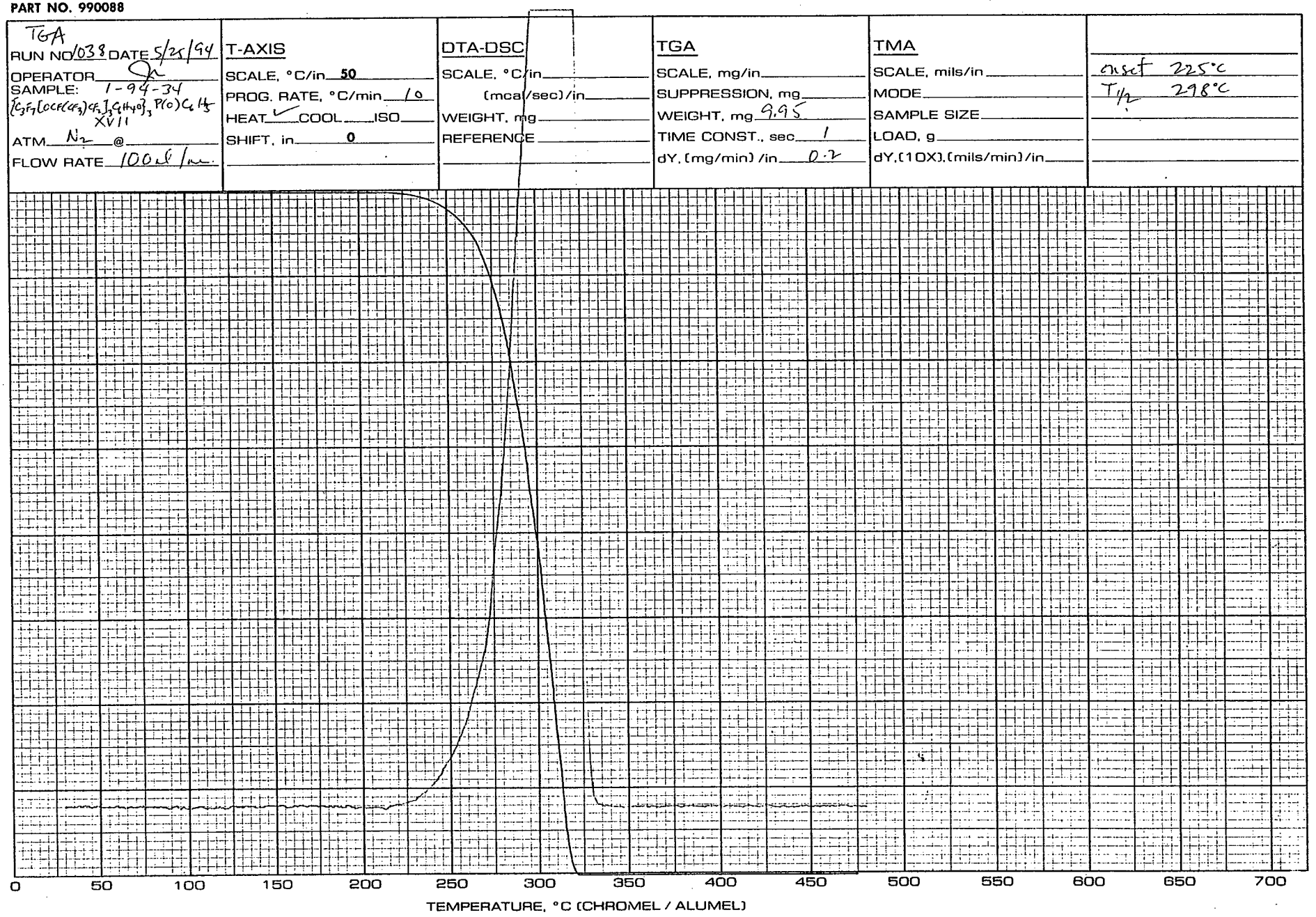


Figure 53. TGA of $\{C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O\}_2P(O)C_6H_5$ (XVII) in N_2.

TABLE 48

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $\{C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O\}_2P(O)C_6H_5$ (MW 1642)

m/e	%	m/e	%	m/e	%	m/e	%	m/e	%
31	28.8	88	5.6	146	5.3	195	7.4	336	5.2
36	19.1	93	5.2	147	26.8	203	7.3	337	6.3
38	10.7	95	6.1	150	21.9	204	52.8	345	5.6
44	5.9	96	7.1	151	7.9	205	11.6	365	5.2
47	31.2	97	33.4	157	6.2	207	5.0	385	10.3
50	29.1	100	30.0	161	6.3	213	9.6	551	5.3
51	15.4	101	6.9	162	19.0	214	20.8	616	6.6
63	5.4	107	6.1	163	5.8	219	10.8	620	6.4
65	6.5	114	11.2	165	10.7	223	29.6	740	13.4
66	12.3	119	67.0	169	93.3	224	33.3	741	7.2
69	100.0	124	5.5	170	11.6	225	8.4	760	7.6
70	7.3	125	8.4	173	6.3	229	5.9	782	5.7
73	8.6	126	17.3	174	14.0	242	6.7	883	10.0
75	8.2	127	11.9	175	6.0	243	10.3	902	19.8
76	6.3	131	12.6	176	5.6	245	5.5	903	8.0
77	26.1	141	5.1	185	5.8	254	27.8	1025	61.6
78	12.4	142	15.3	189	9.1	285	89.2	1026	27.3
79	6.3	143	71.6	192	6.0	286	25.4	1027	9.3
81	15.1	144	13.1	193	7.8	313	14.4		
85	8.8	145	25.9	194	2.8	335	27.9		

Peaks having intensities lower than 5% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e

1025 - $[M - C_3F_7[OCF(CF_3)CF_2]_2OCF(CF_3)]^+$

902 - $[C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OPF(O)C_6H_5]^+$

883 - $[M - C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]^+$

740 - $[M - C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OPF(O)C_6H_5]^+$

285 - $[CF_2C_6H_4PF(O)C_6H_5]^+$

204 - $[CF_2C_6H_3OP(O)_2]^+$

143 - $[CF_2C_6H_4OH]^+$

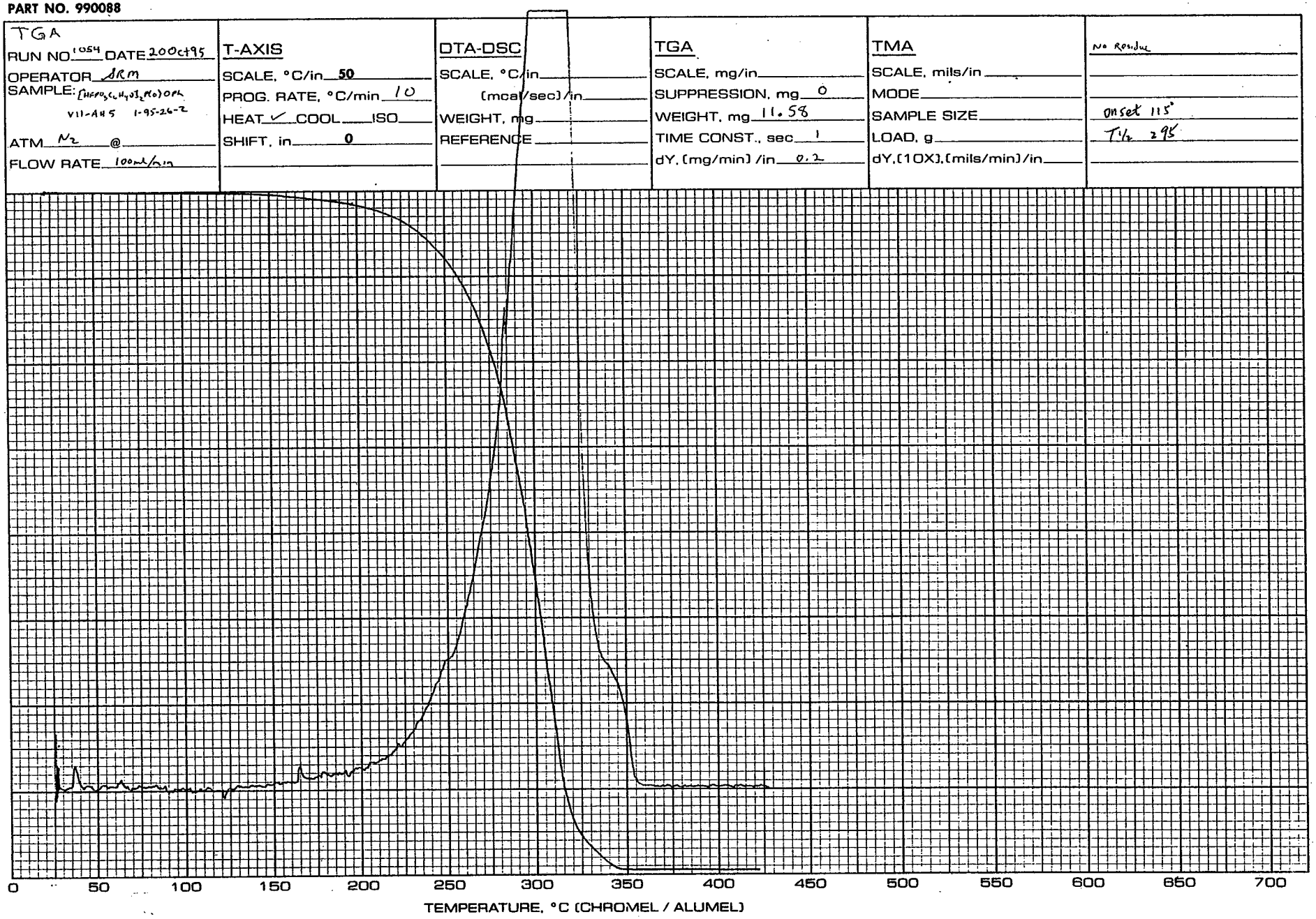


Figure 54. TGA of Additive VII-AS (VII, 66%) in N_2.

conditions using Krytox 143AC fluid (Test 4, Table 4; Test 539, Table 50).

b) By hydrolysis of $[C_3F_7[OCF(CF_3)CF_2]_2]_2C_6H_4O]P(O)OC_6H_5$

A mixture of water (1.05 g) and pure additive VII (5.40 g) was stirred vigorously for 18 h at 95-105°C. After cooling, diethyl ether (30 mL) was added. The organic layer was separated, washed with water (5 x 10 mL), and dried over anhydrous magnesium sulfate. Solvent removal followed by pumping at 50°C for 2 h gave 4.77 g of liquid. Quantitative GC analysis, using $C_2F_5C_6H_4OP(O)(C_6H_5)_2$ as an internal standard, showed the presence of 24% of VII. A portion of the sample (3.6 g) was sublimed at 80-95°C for 6 h to give 2.6 g of viscous residue, which contained 32% of VII. The product (VII-AH2) was fully effective as rust inhibitor (Test 1, Table 4). The rest of the water washed sample (1.17 g) was rewashed with saturated sodium bicarbonate (6 x 5 mL), water (4 x 5 mL) and dried. The recovered material (0.42 g, 33% recovery) which contained 49% of VII, was sublimed at 75-80°C for 3 h. The residue (0.27 g) contained 95% of VII; the material was fully effective as rust inhibitor (Test 10, Table 4).

Preparation of $[C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]_{2-x}P(O)OC_6H_5(OH)_x$ (XVI-AS)

In an inert atmosphere enclosure into a stirred solution of $C_6H_5OP(O)Cl_2$ (2.78 g, 13.2 mmol) in Freon-113 (15 mL) and benzene (25 mL) was added a solution of $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OH$ (15.01 g, 19.75 mmol) and triethylamine (5.0 g, 49 mmol) in Freon-

113 (35 mL) over a period of 3.5 h. After stirring for an additional 0.5 h at room temperature the reaction mixture was heated at 60-65°C under nitrogen bypass for 19 h. Following cooling to room temperature, the precipitated triethylamine hydrochloride (2.8 g) was filtered; evaporation of the filtrate gave a brown liquid (16.95 g) which was dissolved in diethyl ether (100 mL) and washed with water (5 x 25 mL). After drying over anhydrous magnesium sulfate and evaporation in vacuo, 13.81 g of yellow liquid was obtained. The subsequent sublimation (at 90-100°C for 10 h) removed low molecular weight impurities and resulted in 11.9 g of a yellow liquid residue. Quantitative GC analysis, using $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)C_6H_5$ as an internal standard, showed it to contain 87% of $[C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]_2P(O)OC_6H_5$. The TGA is presented in Figure 55; the material provided total rust protection under the CREP conditions using Demnum fluid over the standard 1 h exposure (Test 28, Table 4; Test 695, Table 50) and over a 24 h period (Test 30, Table 4; Test 692, Table 50).

Preparation of $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_{2-x}P(O)C_6H_5(OH)_x$ (VIII-AS)

In an inert atmosphere enclosure into a stirred solution of $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OH$ (1.51 g, 2.52 mmol) and $C_6H_5P(O)Cl_2$ (0.33 g, 1.69 mmol) in Freon-113 (7 mL) was added triethylamine (0.64 g, 6.3 mmol) in benzene (4 mL) over a period of 10 minutes. After stirring for an additional 0.5 h at room temperature, the reaction mixture was heated at 60-65°C under nitrogen bypass for

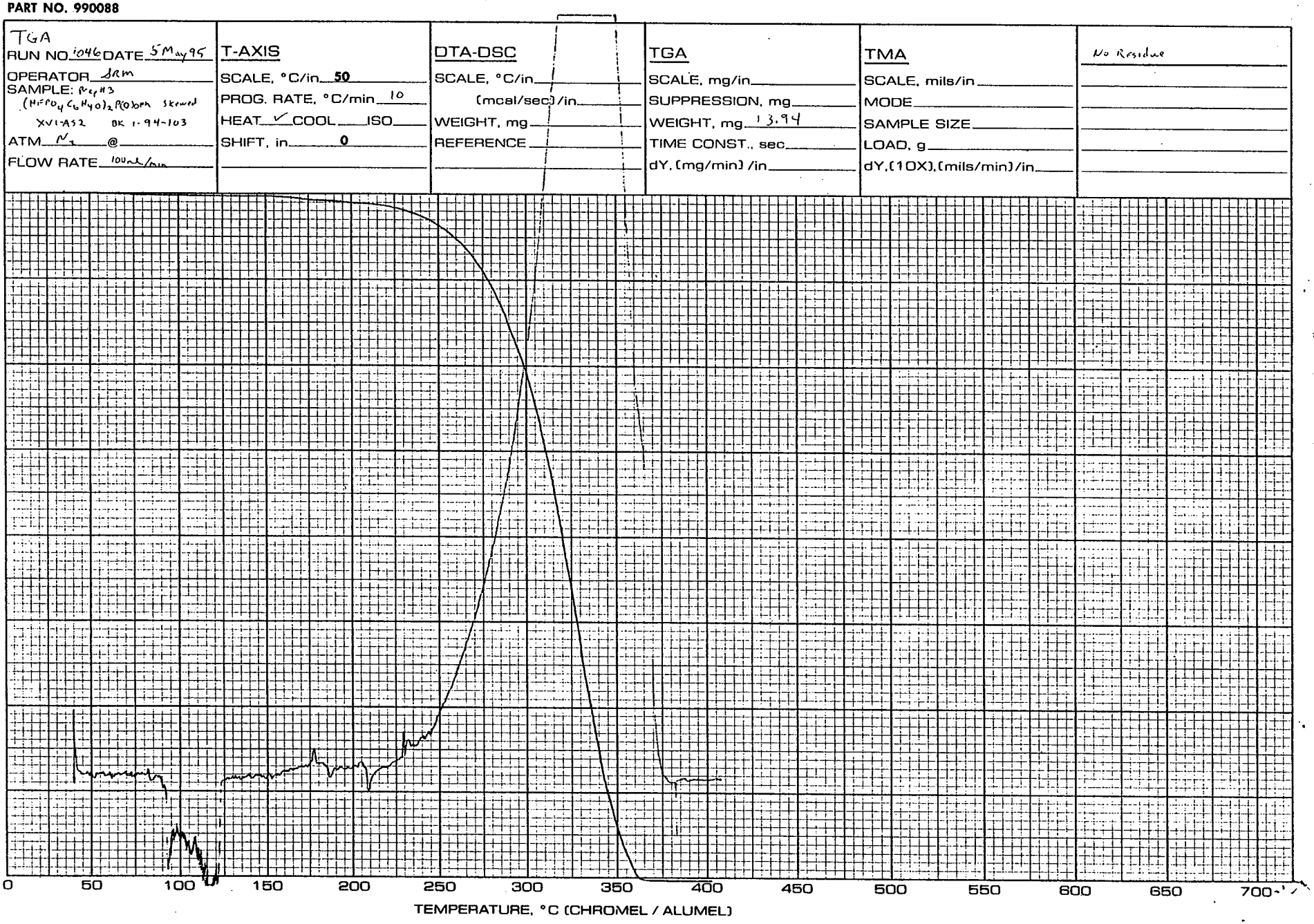


Figure 55. TGA of Additive XVI-AS (XVI, 87%) in N_2.

21 h. Following filtration to separate the precipitated triethylamine hydrochloride, and solvent removal from the filtrate gave a viscous liquid product (1.77 g). The material was dissolved in ether (40 mL), washed with water (3 x 10 mL, 3 x 5 mL), and dried over anhydrous magnesium sulfate, After solvent evaporation 1.54 g of yellow liquid was obtained. Subsequent sublimation at 95°C over 4.5 h resulted in 1.46 g of VIII-AS. Quantitative GC analysis, using $(C_2F_5C_6H_4O)_3P(O)$ as an internal standard, showed 62% of $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)C_6H_5$. The material was almost fully effective under CREP conditions as a corrosion inhibitor both over 1 h and 24 h exposures (Tests 12 and 13 respectively, Table 4).

Preparation of $[C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]_{2-x}P(O)C_6H_5(OH)_x$ (XVII-AS)

In an inert atmosphere enclosure into a stirred solution of $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OH$ (4.0 g, 5.3 mmol) and $C_6H_5P(O)Cl_2$ (0.68 g, 3.5 mmol) in Freon-113 (10 mL) was added triethylamine (1.1 g, 10.5 mmol) in benzene (5 mL) over a period of 0.5 h. After stirring for an additional 0.5 h at room temperature, the reaction mixture was heated at 60°C under nitrogen bypass for 21 h. Following cooling to room temperature, the precipitated triethylamine hydrochloride was filtered off, and the solvents removed <u>in vacuo</u> to give 3.71 g of a light yellow liquid. After exposure to air, a 2 g portion was distilled <u>in vacuo</u> using a short distillation path to give 1.38 g of distillate, (BP 170-179°C/0.001 mm Hg, bath temperature 235-240°C). Quantitative GC

analysis showed 98% of $[C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]_2P(O)C_6H_5$; the material prior to distillation contained 72% of Compound XVII. The undistilled material exhibited some corrosion inhibition with a ranking of 7 (Test 34, Table 4). The distilled portion was more detrimental, insofar as corrosion is concerned, than the fluids Demnum S-100 (Test 35, Table 4) and Fomblin Z25 (Test 37, Table 4) free from an additive.

Hydrolytic Stability Evaluation of 1% Solution of XVI in Demnum S-100

A 1% solution (12.44 g) was prepared by adding Demnum S-100 to 123.1 mg of additive XVI. A mixture of the above solution (10.17 g) and water (2.5 mL) was stirred vigorously in air at 100°C for 24 h. After cooling, the bottom layer was separated and analyzed by GC. The additive VIII, $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)C_6H_5$, was used as an internal standard. To 1.00 g aliquots of the original and the treated solution was added 10.9 mg of VIII. On the basis of GC analysis, presented in Figures 56 and 57, it is apparent that the concentration of XVI was unchanged in the water-treated solution, showing an absence of hydrolysis.

Hydrolytic Stability Evaluation of 1% Solution of XVI-AS5 in Demnum S-100

A 1% solution (9.11 g) was prepared by adding Demnum S-100 to 91.0 mg of XVI-AS5. A mixture of the above solution (7.00 g) and water (1.75 mL) was stirred vigorously in air at

RUN # 12 AUG/17/95 10:48:29
ID 1759

AREA%

RT	AREA	TYPE	AR/HT	AREA%
0.09	516200	D BB	0.069	10.099
3.69	121110	BV	1.260	2.369
11.04	9927	PB	0.632	0.194
13.85	1307500	PV	0.324	25.580
14.53	260510	VV	0.330	5.097
14.89	1237200	VV	0.334	24.203
16.23	1921	VV	0.140	0.038
16.52	10468	VV	0.152	0.205
16.90	2865	VV	0.138	0.056
17.04	2200	VP	0.122	0.043
17.34	18319	PV	0.157	0.358
17.60	5153	VV	0.147	0.101
17.84	3670	VV	0.131	0.072
18.13	28571	VV	0.166	0.559
18.38	7787	D VV	0.152	0.152
18.60	5330	VV	0.144	0.104
18.90	35899	VV	0.179	0.702
19.12	9397	D VV	0.153	0.184
19.34	6646	VV	0.158	0.130
19.62	45450	VV	0.255	0.889
20.33	29127	VV	0.290	0.570
20.98	12281	VP	0.258	0.240
21.62	8434	PV	0.163	0.165
22.28	13841	PB	0.179	0.271
22.93	33553	PV	0.273	0.656
23.57	69624	VV	0.429	1.362
25.31	1308600	I VH	4.334	25.601

TOTAL AREA= 5111600
MUL FACTOR= 1.0000E+00

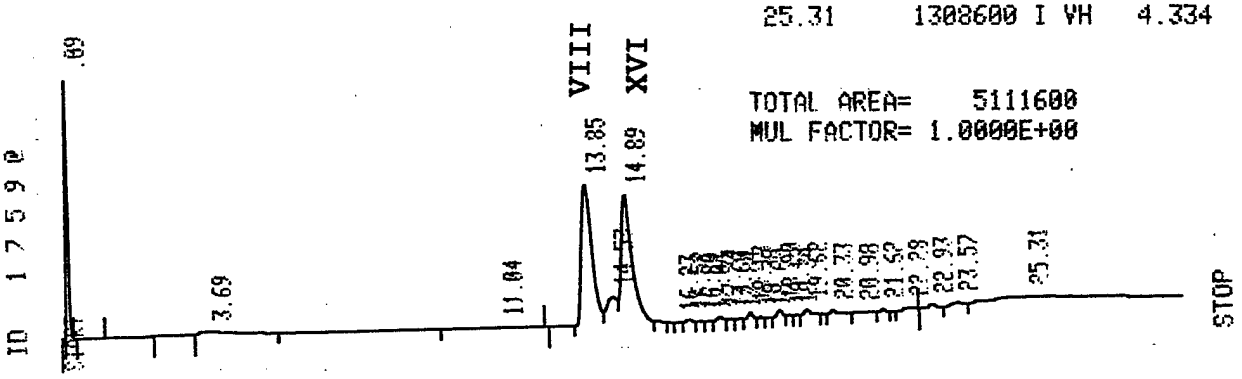


Figure 56. Gas Chromatogram of 1% solution of XVI in Demnum S-100 after treatment with water in air at 100°C for 24 h (contains 1.08% of VIII as an internal standard; GC Ratio XVI/VIII = 0.946).

RUN # 16 AUG/17/95 14:56:37
ID 1762

AREA%

RT	AREA	TYPE	AR/HT	AREA%
0.08	27251	D PB	0.067	1.084
4.07	66100	BB	1.281	2.629
11.59	1539	PB	0.187	0.061
13.92	589300	PV	0.325	23.439
14.62	157680	VV	0.345	6.272
14.97	556450	VB	0.384	22.133
16.53	4259	BV	0.158	0.169
17.05	851	PP	0.114	0.034
17.33	8346	PV	0.148	0.332
17.60	2147	VP	0.127	0.085
17.84	2062	PP	0.114	0.082
18.12	20447	PV	0.149	0.813
18.38	4170	VP	0.122	0.166
18.61	3828	PP	0.112	0.152
18.92	42850	PV	0.162	1.704
19.15	7646	VV	0.133	0.304
19.36	5305	VP	0.122	0.211
19.70	68023	PV	0.176	2.706
19.91	13805	D VV	0.138	0.549
20.10	6918	D VV	0.130	0.275
20.45	83756	VV	0.186	3.331
20.64	15242	D VV	0.129	0.606
20.82	4615	D VV	0.114	0.184
21.16	92399	VV	0.188	3.675
21.33	12507	D VV	0.112	0.498
21.51	2951	D VV	0.100	0.117
21.85	109710	VV	0.217	4.364
22.53	115970	VB	0.219	4.613
23.16	122200	BV	0.252	4.861
23.76	121410	VV	0.295	4.829
24.33	110940	VV	0.405	4.413
24.84	133460	VB	0.821	5.303

TOTAL AREA= 2514100
MUL FACTOR= 1.0000E+00

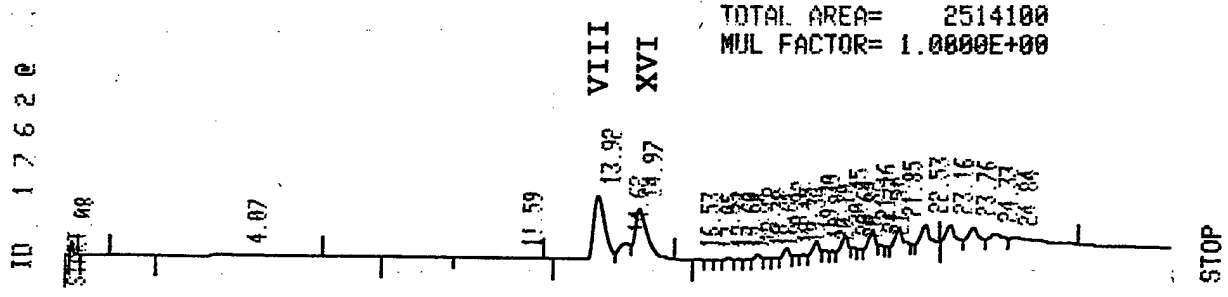


Figure 57. Gas chromatogram of 1% solution of XVI in Demnum S-100 (contains 1.08% of VIII as an internal standard; GC Ratio XVI/VIII = 0.944).

100°C for 24 h. After cooling, the bottom layer was separated and dried over anhydrous magnesium sulfate to give 5.26 g of a clear solution. The GC analysis was performed using $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)C_6H_5$ (VIII), as an internal standard. To 1.0 g aliquots of the original and treated solutions was added 11.0 mg of VIII. The gas chromatograms given in Figures 58 and 59 showed the ratios of XVI/VIII of 0.583 and 0.430 respectively. A control solution containing 11.0 mg of VIII, 10 mg of pure XVI and 990 mg of Demnum S-100 was analyzed by GC; the ratio of XVI/VIII was found to be 0.735 as shown in Figure 60. Based on the above data, the content of XVI in the original 1% solution of XVI-AS5 in Demnum S-100 was 0.79%; following water treatment, it was reduced to 0.59%. It would appear that XVI-AS5 is more susceptible to hydrolysis in Demnum S-100 than pure XVI.

Hydrolytic Stability Evaluation of 1% Solution of Additive VII in Demnum S-100

A 1% solution (8.36 g) was prepared by adding Demnum S-100 to 83.2 mg of Additive VII. A mixture of the above solution (6.01 g) and water (1.5 mL) was stirred vigorously in air at 100°C for 24 h. After cooling, the bottom layer was separated, dried over anhydrous magnesium sulfate, and analyzed by GC using Additive XVI, $[C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]_2P(O)OC_6H_5$, as the internal standard. To 1.01 g aliquots of the original and the treated solution was added 11.7 mg of XVI. The gas chromatograms given in

RUN # 10 JUN/06/96 09:59:59
ID 1982

AREA%

RT	AREA	TYPE	AR/HT	AREA%
0.08	165350	D BB	0.063	3.345
5.60	16602	PP	1.305	0.336
12.97	0	PP	0.000	0.000
14.03	1765100	PB	0.325	35.706
15.06	1029900	BV	0.280	20.833
16.26	2290	PP	0.119	0.046
16.57	15817	PV	0.140	0.320
16.85	8487	VV	0.155	0.172
17.08	6515	VP	0.144	0.132
17.41	30530	PV	0.147	0.618
17.66	6566	VV	0.124	0.133
17.90	5130	VP	0.117	0.104
18.22	46799	PV	0.171	0.947
18.45	9651	D VV	0.146	0.195
18.68	6241	VV	0.147	0.126
19.00	61114	VV	0.308	1.236
19.38	16641	VV	0.180	0.337
19.71	63434	VV	0.196	1.283
19.94	33005	VV	0.165	0.668
20.13	39417	VV	0.183	0.797
20.55	176400	VV	0.241	3.568
20.75	66924	VV	0.158	1.354
20.93	61051	D VV	0.164	1.235
21.29	338220	VV	0.292	6.842
21.55	83006	D VV	0.129	1.679
21.71	75869	D VV	0.142	1.535
22.13	452180	VV	0.366	9.147
22.64	134670	VB	0.193	2.724
24.65	12777	PV	0.301	0.259
25.18	41386	VV	0.437	0.837
25.79	172410	VB	1.730	3.488

TOTAL AREA= 4943500
MUL FACTOR= 1.0000E+00

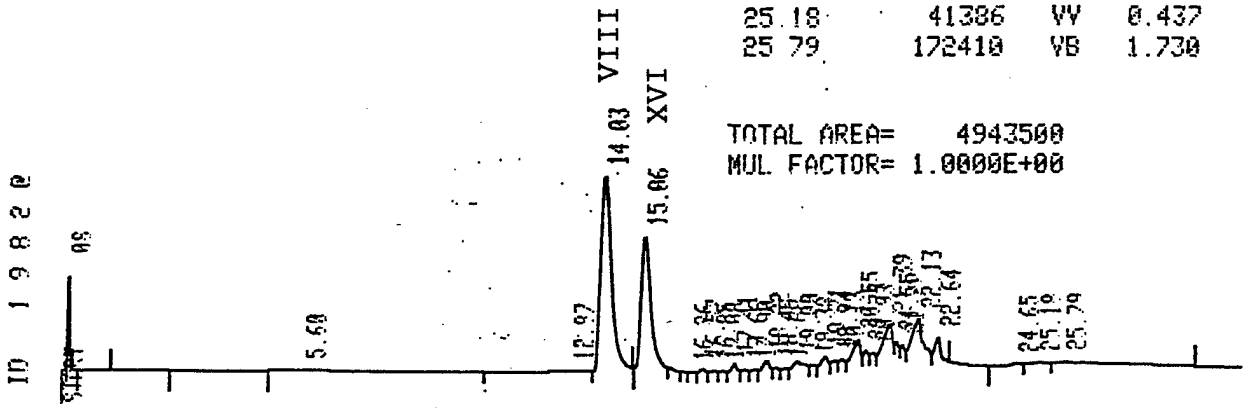


Figure 58. Gas chromatogram of 1% solution of XVI-AS5 in Demnum S-100 (contains 1.10% of VIII as an internal standard; GC Ratio XVI/VIII = 0.583).

RUN # 7 JUN/05/96 09:48:24
ID 1979

AREA%

RT	AREA	TYPE	AR/HT	AREA%
0.08	151910	D BB	0.063	3.221
4.46	223660	PB	1.809	4.742
12.67	14733	PV	0.515	0.312
14.00	2240900	VV	0.330	47.512
15.03	964450	VV	0.309	20.449
15.97	8105	D VV	0.169	0.172
16.23	4786	VP	0.145	0.102
16.54	20241	PV	0.136	0.429
16.82	10295	VV	0.149	0.218
17.06	8644	VP	0.143	0.183
17.40	42151	PV	0.146	0.894
17.64	10545	VV	0.119	0.224
17.87	9128	VP	0.119	0.194
18.23	76747	PV	0.167	1.627
18.45	17690	VV	0.129	0.375
18.66	12350	VP	0.125	0.262
19.04	97638	PV	0.185	2.070
19.23	21436	D VV	0.131	0.455
19.42	10562	D VP	0.126	0.224
19.77	74463	PB	0.218	1.579
20.38	21042	PV	0.160	0.446
20.57	12807	D VV	0.154	0.272
20.76	8604	D VV	0.146	0.182
21.09	60392	VV	0.183	1.280
21.30	20443	VV	0.152	0.433
21.45	17248	D VV	0.150	0.366
21.83	133430	VV	0.236	2.829
21.99	41425	D VV	0.139	0.878
22.53	254770	VV	0.366	5.402
23.06	125880	VV	0.274	2.669

TOTAL AREA= 4716500
MUL FACTOR= 1.0000E+00

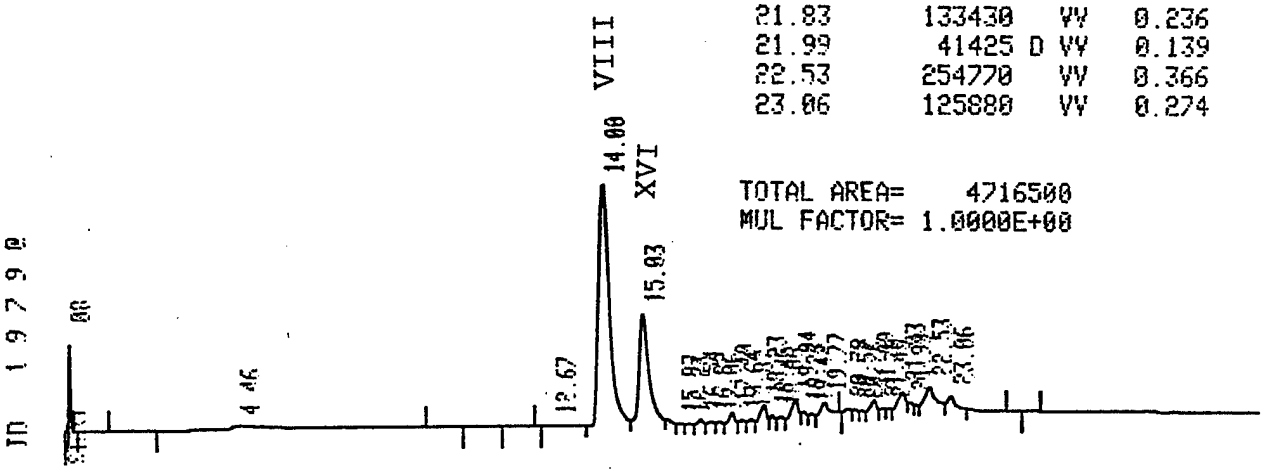


Figure 59. Gas Chromatogram of a 1% solution of XVI-AS5 in Demnum S-100 after treatment with water in air at 100°C for 24 h (contains 1.40% of VIII as an internal standard; GC Ratio XVI/VIII = 0.430).

RUN # 14 JUN/07/96 11:23:28
ID 1985 (b)

AREA%

RT	AREA	TYPE	AR/HT	AREA%
0.09	258880	D BB	0.064	4.591
13.99	1871700	PV	0.321	33.189
15.02	1376400	VB	0.264	24.407
16.24	2192	BP	0.118	0.039
16.54	15541	PV	0.140	0.276
16.83	6891	VV	0.153	0.122
17.06	6395	VP	0.148	0.113
17.38	29925	PV	0.154	0.531
17.63	8360	VV	0.147	0.148
17.87	8211	VV	0.154	0.146
18.18	48819	VV	0.204	0.866
18.64	11693	VV	0.176	0.207
18.92	37384	VV	0.225	0.663
19.34	26273	VV	0.192	0.466
19.66	78980	VV	0.212	1.401
19.90	38639	VV	0.168	0.685
20.09	50272	VV	0.190	0.891
20.50	198630	VV	0.254	3.522
20.70	73109	J VV	0.158	1.296
20.87	67600	D VV	0.166	1.199
21.30	307770	VV	0.283	5.457
21.45	75497	D VV	0.125	1.339
21.60	67683	D VV	0.141	1.200
21.96	312340	VV	0.308	5.538
22.53	253930	VV	0.328	4.503
23.01	138990	VV	0.326	2.465
24.62	49793	VV	0.413	0.883
25.17	93161	VV	0.580	1.652
25.76	124420	VB	1.089	2.206

TOTAL AREA= 5639500
MUL FACTOR= 1.0000E+00

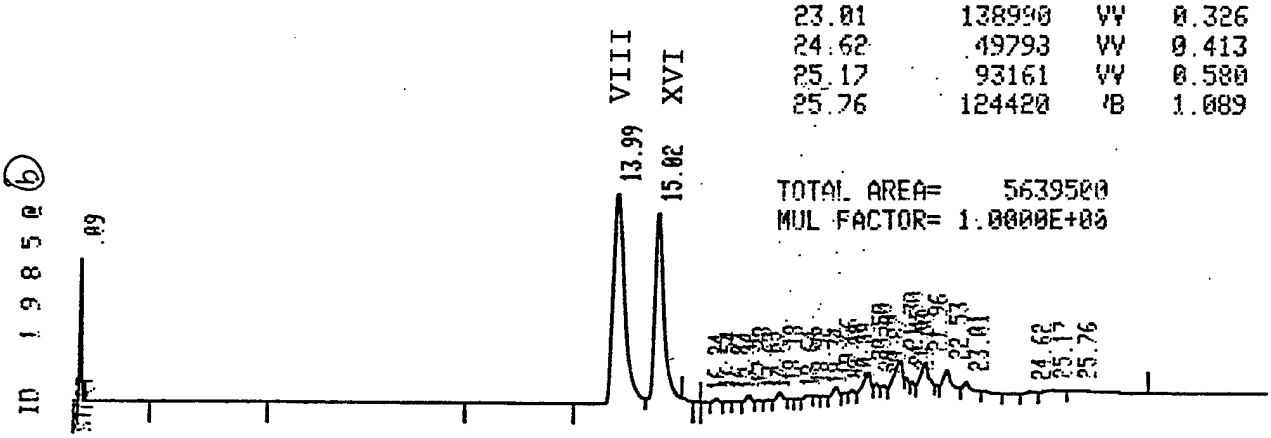


Figure 60. Gas chromatogram of a 1% solution of XVI in Demnum S-100 (contains 1.40% of VII as an internal standard; GC Ratio XVI/VIII = 0.735).

Figures 61 and 62 show the respective ratios of VII/XVI as 0.778 and 0.902; this corresponds to 86% recovery of VII.

General Procedure for Determining the Hydrolytic Stability of Phosphate/Phosphonate Additives

A mixture of an additive (200-250 mg) and water (5 mL) was heated at 100°C for 24 h while stirred vigorously. After cooling, the mixture was extracted with ether (3 x 10 mL), dried over $MgSO_4$ and the solvent evaporated in vacuo. To determine starting material recovery, the residue was then subjected to quantitative GC analysis using an appropriate internal standard. The results of these evaluations are summarized in Table 3.

Thermal Oxidative Degradation Procedure

All the tests were carried out in pure oxygen (~400 mm Hg pressure at 25°C) in the presence of M-50, Pyrowear 675 and Ti(6Al,4V) alloys over 24 h or other specified periods at denoted temperatures. At the end of exposure the volatile condensables were removed in vacuo and weighed. Detailed descriptions of the procedure and apparatus were reported previously [Ref. 11]. The temperature at which the total of volatile condensables amounted to $\geq$0.50 mg/g (mg of products formed per g of fluid employed) was defined as the degradation onset.

All the tests performed under subject contract are compiled in Table 49.

RUN # 1 APR/22/96 10:23:00
ID 1941

AREA%

RT	AREA	TYPE	AR/HT	AREA%
0.06	142250	D BB	0.064	2.916
3.12	51485	PV	0.457	1.055
3.55	88630	VB	0.853	1.817
12.05	4526	PP	0.452	0.093
12.89	1916	PP	0.296	0.039
13.51	1567100	PB	0.325	32.117
14.49	2692	PV	0.119	0.055
14.84	2015200	VB	0.260	41.302
16.06	3037	PP	0.118	0.062
16.37	24385	PV	0.148	0.500
16.65	17861	VV	0.177	0.366
16.88	10282	VP	0.147	0.211
17.21	47109	PV	0.146	0.966
17.46	11178	VV	0.119	0.229
17.70	13564	VV	0.135	0.278
18.05	91153	VV	0.172	1.868
18.27	19333	VV	0.125	0.396
18.48	13757	VV	0.120	0.282
18.87	134600	VV	0.190	2.759
19.05	32956	D VV	0.134	0.675
19.25	21296	D VV	0.139	0.437
19.62	135690	VV	0.199	2.781
19.79	32270	D VV	0.128	0.661
19.95	22060	D VV	0.140	0.452
20.26	85621	VB	0.237	1.755
20.91	2349	BB	0.068	0.048
23.53	1995	PB	0.289	0.041
26.84	284950	BV	2.820	5.840

TOTAL AREA= 4879200
MUL FACTOR= 1.0000E+00

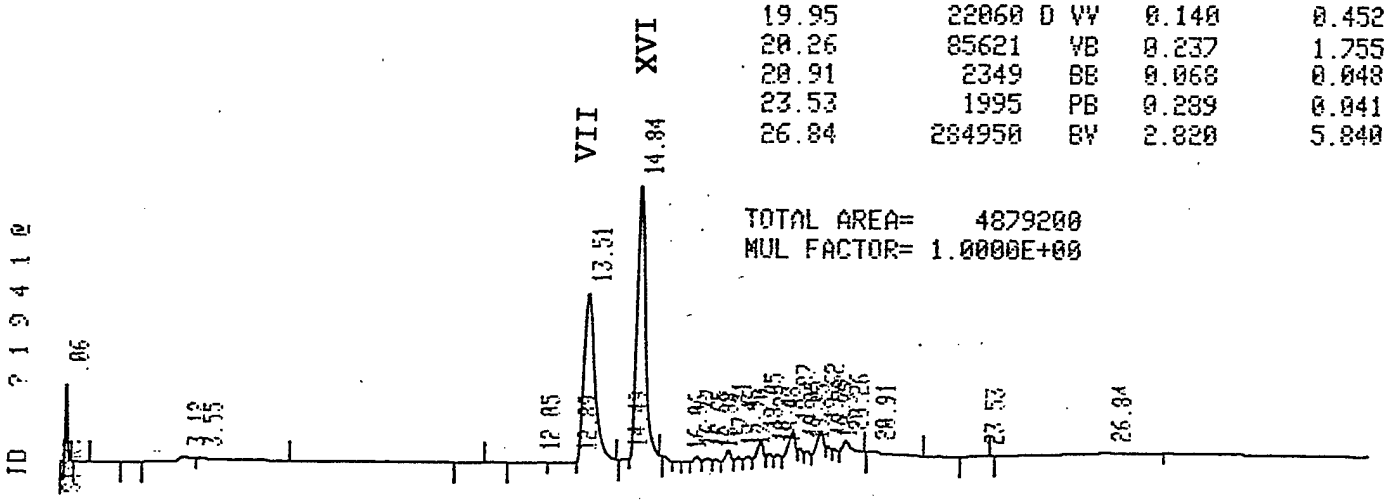


Figure 61. Gas Chromatogram of 1% solution of VII in Demnum S-100 after treatment with water in air at 100°C for 24 h (contains 1.15% of XVI as an internal standard; GC Ratio VII/XVI = 0.778).

RUN # 1 APR/19/96 13:10:37
ID 1939

AREA%

RT	AREA	TYPE	AR/HT	AREA%
0.05	180410	D BB	0.065	2.859
1.88	24100	PV	0.771	0.382
3.26	146050	VV	0.910	2.315
12.06	4847	PP	0.662	0.077
12.92	4604	PP	0.291	0.073
13.53	1940600	PB	0.314	30.755
14.87	2152300	PB	0.257	34.110
16.07	3033	PP	0.116	0.048
16.38	28262	PV	0.152	0.448
16.65	32559	VV	0.207	0.516
16.87	15225	D VV	0.155	0.241
17.22	53551	VV	0.151	0.849
17.47	18845	VV	0.141	0.299
17.71	31351	VV	0.170	0.497
18.07	128180	VV	0.200	2.031
18.29	35845	VV	0.144	0.568
18.51	33949	VV	0.154	0.538
18.91	210710	VV	0.217	3.339
19.10	63450	D VV	0.147	1.006
19.30	53985	D VV	0.161	0.856
19.72	263490	VV	0.243	4.176
19.88	82826	D VV	0.139	1.313
20.05	69081	D VV	0.153	1.095
20.42	299890	VV	0.299	4.753
20.72	56864	D VV	0.145	0.901
20.97	225690	VV	0.474	3.577
22.61	56248	VV	0.588	0.891
23.47	26314	VV	0.534	0.417
24.32	17272	VV	0.502	0.274
25.08	22053	VV	0.595	0.350
25.98	27316	VB	0.929	0.433
28.00	941	D PP	0.077	0.015

TOTAL AREA= 6309800
MUL FACTOR= 1.0000E+00

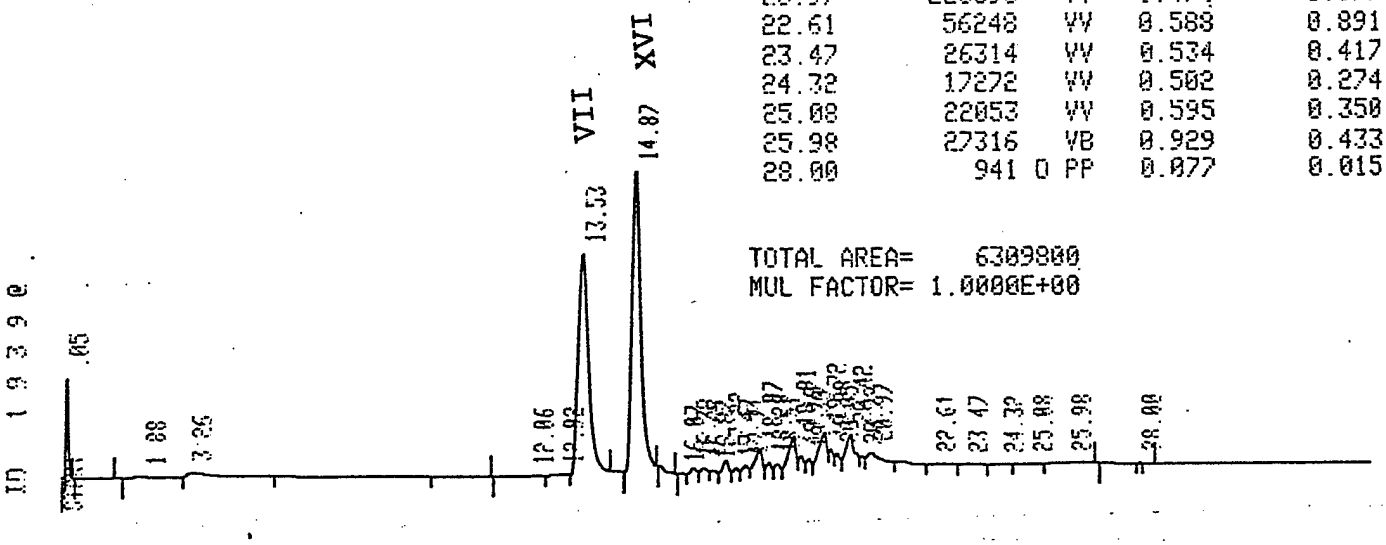


Figure 62. Gas chromatogram of 1% solution of VII in Demnum S-100 (contains 1.15% of XVI as an internal standard; GC Ratio VII/XVI = 0.902).

TABLE 49

EFFECT OF ADDITIVES ON PERFLUOROPOLYALKYLETHER FLUID THERMAL OXIDATIVE DEGRADATION[a]

Test No.	Fluid Type	Fluid g	Additive[b]	Metal	Temp °C	Volatiles mg	Volatiles mg/g	Metal Wt Chg mg/cm^2	Metal Appearance
1	Krytox 143AC	3.02	None	M-50	316	130.8	43.3	+0.36	dark grey
2	Krytox 143AC	3.03	II	M-50	316	2.9	0.96	-0.06	shiny/discolored
3	Krytox 143AC	3.07	I	M-50	316	1.0	0.32	0.0	shiny
4	Krytox 143AC	2.91	V	M-50	316	0.6	0.21	0.0	shiny/discolored
5	Fomblin Z25-P28	3.02	I	M-50	316	2.2	0.73	-0.12	shiny/black spots
6	Fomblin Z25-P28	3.10	V	M-50	316	0.8	0.26	+0.06	shiny/black spots
7	Brayco 814Z	3.14	I	M-50	316	9.0	2.87	+1.37	dull/black spots
8	Brayco 814Z	3.04	V	M-50	316	1.1	0.36	+0.84	½ shiny/½ discolor
9	Krytox 143AC	2.96	VIII	M-50	316	0.1	0.03	0.0	shiny/part discolor
10	Fomblin Z25-P28	3.02	VIII	M-50	316	534.4	176.9	-5.2	flaky corrosion
11	Krytox 143AC	3.11	VI	M-50	316	0.8	0.26	0.0	shiny/bronze color
12	Fomblin Z25-P28	3.34	VI	M-50	316	41.3	12.4	-8.4	flaky corrosion
13	Krytox 143AC	2.98	IX	M-50	316	0.4	0.13	0.0	shiny/yellow color
14	Fomblin Z25-P28	3.09	IX	M-50	316	35.7	11.6	-1.25	dark grey/rough

TABLE 49 (continued)

EFFECT OF ADDITIVES ON PERFLUOROPOLYALKYLETHER FLUID THERMAL OXIDATIVE DEGRADATION[a]

Test No.	Fluid Type	Fluid g	Additive[b]	Metal	Temp °C	Volatiles mg	Volatiles mg/g	Metal Wt Chg mg/cm^2	Metal Appearance
15	Krytox 143AC	3.03	X	M-50	316	0.4	0.13	0.0	shiny/brown color
16	Fomblin Z25-P28	3.09	X	M-50	316	409.1	132.4	-4.8	flaky corrosion
17	Krytox 143AC	3.26	VII	M-50	316	0.8	0.25	0.0	brown discoloration
18	Fomblin Z25-P28	3.13	VII	M-50	316	165.5	52.9	-0.36	black/corroded edge
19	Krytox 143AC	3.06	V	M-50	330	1.0	0.33	+0.06	brown discoloration
20	Fomblin Z25-P28	3.12	V	M-50	330	102.7	32.9	-10.2	flaky corrosion
21	Krytox 143AC	3.18	XI	M-50	316	1.0	0.31	+0.24	dark grey
22	Fomblin Z25-P28	3.21	XI	M-50	316	3.9	1.21	+0.30	shiny/some black spots
23	Fomblin Z25-P28	3.07	V	M-50	325	36.6	11.9	-6.8	flaky corrosion
24	Krytox 143AC	2.96	XIII	M-50	316	1.0	0.34	+0.06	part shiny
25	Fomblin Z25-P28	3.00	XIII	M-50	316	13.2	4.4	-3.11	part corroded
26	Krytox 143AC	3.33	XII	M-50	316	0.8	0.24	0.0	brown discoloration
27	Fomblin Z25-P151	3.14	XII	M-50	316	1.6	0.51	-0.06	dark grey
28	Fomblin Z25-P151	3.17	PH-3	M-50	316[c]	1.1	0.35	+0.06	slightly shiny

TABLE 49 (continued)

EFFECT OF ADDITIVES ON PERFLUOROPOLYALKYLETHER FLUID THERMAL OXIDATIVE DEGRADATION[a]

Test No.	Fluid Type	Fluid g	Additive[b]	Metal	Temp °C	Volatiles mg	Volatiles mg/g	Metal Wt Chg mg/cm^2	Metal Appearance
29	Demnum S-100	3.11	VIII	M-50	330	0.5	0.16	0.0	shiny/some spots
29A	Demnum S-100	3.14	VIII	M-50	330	2.8	0.89	0.0	shiny/brown color
30	Krytox 143AC	3.00	VIII	M-50	330	1.8	0.60	-0.18	shiny/some spots
31	Krytox 143AC	3.04	XVI	M-50	316	0.2	0.07	-0.06	shiny
32	Fomblin Z25-P151	3.26	XVI	M-50	316	0.8	0.24	-0.18	shiny
33	Krytox 143AC	3.04	XVII	M-50	316	0.7	0.23	-0.06	part shiny/uneven color
34	Fomblin Z25-P151	3.14	XVII	M-50	316	0.3	0.10	+0.18	shiny/brown color
35	Krytox 143AC	2.89	XVI-AS1[d]	M-50	316	3.5	1.21	-0.24	dull black
36	Fomblin Z25-P151	3.15	XVI-AS1[d]	M-50	316	6.1	1.94	-1.02	flaky corrosion
37	Demnum S-100	3.07	XVI-AS1[d]	M-50	316	0.1	0.03	-0.12	shiny/some spots
38	Krytox 143AC	3.01	XVI-AS1[d]	M-50	330	8.5	2.82	-3.28	flaky corrosion
39	Fomblin Z25-P151	3.17	XVI-AS1[d]	M-50	330	3379	1066	-7.41	flaky corrosion
40	Demnum S-100	3.26	XVI-AS1[d]	M-50	330	21.7	6.66	-1.49	dark and corroded
41	Krytox 143AC	2.98	XVII-AS[d]	M-50	316	0.7	0.23	+0.18	dull dark grey

TABLE 49 (continued)

EFFECT OF ADDITIVES ON PERFLUOROPOLYALKYLETHER FLUID THERMAL OXIDATIVE DEGRADATION[a]

Test No.	Fluid Type	Fluid g	Additive[b]	Metal	Temp °C	Volatiles mg	Volatiles mg/g	Metal Wt Chg mg/cm^2	Metal Appearance
42	Demnum S-100	3.06	XVII-AS[d]	M-50	316	0.6	0.20	+0.06	dull dark grey
43	Fomblin Z25-P151	3.09	XVII-AS[d]	M-50	316	77.5	25.08	-3.58	flaky corrosion
44	Demnum S-100	3.09	XVI	M-50	330	0.7	0.23	+0.24	shiny/brown spot
44B	Demnum S-100	3.28	XVI	M-50	330	0.9	0.27	+0.72	½ black/½ shiny
45	Demnum S-100	3.14	VII	M-50	316	0.5	0.16	-0.06	slightly dull
46	Demnum S-100	3.17	XVI-AS3[e]	M-50	330	3.1	0.98	+0.36	brown discoloration
47	Demnum S-100	3.06	none	Ti(6Al,4V)	316	483.1	157.9	+0.06	dull dark brown
48	Demnum S-100	3.06	none	Pyrowear675	330	93.6	30.6	+0.18	½ black/½ shiny
49	Krytox 143AC	3.05	none	Ti(6Al,4V)	316	911.9	299.0	+0.24	dull dark brown
50	Krytox 143AC	3.00	XVI	Ti(6Al,4V)	316	1.2	0.40	+0.06	shiny/small spots
51	Demnum S-100	2.96	XVI	Ti(6Al,4V)	330	0.5	0.17	+0.06	shiny/discolored
52	Demnum S-100	3.30	XVI	Pyrowear675[f]	330	1.5	0.45	-	½ brown/½ dark grey
53[g]	Demnum S-100	3.30	XVI	Pyrowear675	330	1.7	0.52	+0.20	dull dark grey
54	Demnum S-100	3.18	XVI(0.5%)	M-50	330	3.4	1.07	+0.30	shiny/black ring

TABLE 49 (continued)

EFFECT OF ADDITIVES ON PERFLUOROPOLYALKYLETHER FLUID THERMAL OXIDATIVE DEGRADATION[a]

Test No.	Fluid Type	Fluid g	Additive[b]	Metal	Temp °C	Volatiles mg	Volatiles mg/g	Metal Wt Chg mg/cm^2	Metal Appearance
55	Demnum S-100	3.09	none	Ti(6Al,4V)	330	1223	395.7	+0.12	dull grey
56	Demnum S-100	3.04	none	2 x M-50	330	297.0	97.7	+0.98[h]	dull/dark brown
57[i]	Demnum S-100	3.05	XVI	M-50	330	40.7	13.3	-0.48	flaky corrosion
58[i]	Demnum S-100	3.04	VIII	M-50	330	18.2	5.99	+0.12	uneven corrosion
59	Demnum S-100	2.98	VIII	Ti(6Al,4V)	330	3.9	1.31	+0.12	shiny
60	Demnum S-100	3.05	VII	M-50	330	2.4	0.79	+0.06	shiny brown/spots
61	Demnum S-100	3.10	VII-AH5	M-50	330	1.5	0.48	0.0	shiny/discolored
62	Demnum S-100	3.09	XVI	2 x M-50	330	2.1	0.68	+0.27[j]	top shiny bottom ½ shiny
63	Demnum S-100	3.11	XVI(1.5%)	M-50	330	0.7	0.22	-	shiny/discolored
64[k]	Demnum S-100	3.11	XVI(1.5%)	M-50	330	7.0	2.25	-2.09	dark/rough corrosion
65	Demnum S-100	3.12	XVI-AS5	M-50	330	1.3	0.42	+0.42	black
66	Demnum S-100	3.11	VIII-AS	M-50	330	3.2	1.03	+0.06	shiny/brown spots
67[i]	Demnum S-100	3.11	XVI(1.5%)	M-50	330	8.5	2.73	-5.50	flaky corrosion
68	Demnum S-100	3.12	XVI-AS5	Ti(6Al,4V)	330	0.8	0.26	0.0	shiny/brown edge

TABLE 49 (continued)

EFFECT OF ADDITIVES ON PERFLUOROPOLYALKYLETHER FLUID THERMAL OXIDATIVE DEGRADATION[a]

Test No.	Fluid Type	Fluid g	Additive[b]	Metal	Temp °C	Volatiles mg	Volatiles mg/g	Metal Wt Chg mg/cm^2	Metal Appearance
69[i]	Demnum S-100	3.11	VIII(1.5%)	M-50	330	20.1	6.46	+0.12	dark/corrosion spots
70[l]	Demnum S-100	3.03	VIII	M-50	330	1.0	0.33	-0.06	shiny/discolored
71[l]	Demnum S-100	3.08	XVI	M-50	330	1.2	0.39	0.0	shiny/discolored
72[l]	Demnum S-100	3.09	XVI-AS5	M-50	330	1.1	0.36	+0.24	shiny/¼ black
73[l]	Demnum S-100	3.15	VII-AH5	M-50	330	1.2	0.38	+0.12	½ shiny/½ black
74	Demnum S-100	3.04	XVI-AS6	M-50	330	1.0	0.33	+0.12	shiny/discolored
75	Demnum S-100	3.13	VIII[m]	M-50	330	1.2	0.38	0.0	shiny/discolored
76	Krytox 143AC	3.04	XVI[m]	M-50	330	1.1	0.36	0.0	shiny/discolored

a) All tests were performed in pure oxygen over a 24 h period using the modified scaled-down, sealed version of the AFML Micro-O-C-Test arrangement.
b) Additive when present was at a 1% by weight concentration unless noted otherwise.
c) This test was performed for a 16 h period.
d) This sample contains an ingredient that is active in the CREP test and the proportion predetermined in the synthesis process.
e) This sample was composed of 50% of XVI-AS2 and 50% of XVI.
f) Pyrowear 675 ball was cleaned by wiping with Freon-113 then ultrasonically cleaned in Freon 113 for 5 minutes.
g) Fluid and Pyrowear 675 ball bearing from Test 52 used for this Test.

TABLE 49 (concluded)

EFFECT OF ADDITIVES ON PERFLUOROPOLYALKYLETHER FLUID THERMAL OXIDATIVE DEGRADATION[a]

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h) This is the average value of the two M-50 coupons used in this test. The two coupons were separated by a 4 mm glass spacer. The top coupon gained 1.31 mg/cm^2 and the bottom coupon gained 0.66 mg/cm^2.
i) This test was conducted over a 48 h period.
j) This is the average value of the two M-50 coupons used in this test. The two coupons were separated by a 4 mm glass spacer. The top coupon gained 0.24 mg/cm^2 and the bottom coupon gained 0.30 mg/cm^2.
k) Fluid and coupon from Test 63 used for this test.
l) The fluid used for this test was formulated 6 months prior to testing.
m) Additive batches which were sent to WL/MLBT to be evaluated.

Corrosion Resistance Evaluation Procedure (CREP)

The operation employed followed in general the original procedure of Warner et al. [Ref. 14] with modifications described by Paciorek et al. [Ref. 15]. All the CREP tests carried out under subject contract are compiled in Table 50.

Shelf Life Stability/Effectiveness Evaluation

To determine shelf life stability of the most promising thermal oxidative degradation inhibitors, 1% solutions of Additives VIII, $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)C_6H_5$ and XVI, $[C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]_2P(O)OC_6H_5$, in Demnum S-100 were stored over a period of 6 months at room temperature. No change in appearance was noted, no clouding or precipitation took place. Thermal oxidative stability determinations, in the presence of M-50 at 330°C over 24 h, were performed on the fresh formulations and after the 6 months exposure. Additive VIII solution: fresh 0.16 mg/g (Test 29); after 6 months, 0.33 mg/g (Test 70). Additive XVI solution: fresh, 0.27 mg/g (Test 44B); after 6 months, 0.39 mg/g (Test 71). All the tests are summarized in Table 49.

To determine the shelf life stability of the most promising corrosion/thermal oxidative degradation inhibitors 1% solutions of Additives VII-AH5, $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_{2-x}P(O)OC_6H_5(OH)_x$ (concentration of VII, 91%), and XVI-AS5, $[C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]_{2-x}P(O)OC_6H_5(OH)_x$ (concentration of XVI, 85%) in Demnum S-100 were stored over a

TABLE 50

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

Test No.	Fluid	Additive Type[a]	Wt.%	Wt. Change mg	A%/B%	Ranking[b]
441	Brayco 814Z	None	-	+0.6	1/5	9+
442	Krytox 143AC	None	-	-1.9	80/60	0
443	Fomblin Z25-P28	None	-	-0.6	80/50	1
444	Brayco 814Z	None	-	-0.2	5/10	9
445	Krytox 143AC	None	-	-0.2	70/60	0
446	Fomblin Z25-P28	$(R_f')_2P(O)Ph$ VIII-AI[c] (3-92-63)	0.6	+0.4	3/3	9+
447	Brayco 814Z	None	-	+1.3	1/4	9+
448	Krytox 143AC	None	-	+0.1	65/45	0
449	Fomblin Z25-P28	$(R_f')_2P(O)OPh$ VII-AI[c] (3-92-59)	0.5	+0.5	3/3	9
450	Brayco 814Z	None	-	-0.4	5/10	9
451	Krytox 143AC	None	-	-0.8	55/45	0
452	Krytox 143AC	$(R_f')_2P(O)Ph$ VIII-AI[c] (3-92-63)	0.5	-0.5	60/65	-3

TABLE 50 (continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

Test No.	Fluid	Additive Type[a]	Wt.%	Wt. Change mg	A%/B%	Ranking[b]
453	Brayco 814Z	None	-	-0.8	35/10	7
454	Krytox 143AC	None	-	-0.9	80/75	0
455	Krytox 143AC	$(R_f')_2P(O)OPh$ VII-AI[c] (3-92-59)	0.5	-0.2	25/30	6
456	Brayco 814Z	None	-	+0.4	10/20	8
457	Krytox 143AC	None	-	-0.2	80/70	0
458	Krytox 143AC	$C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OH$ (3-92-87)	0.5	-0.5	80/60	1
459	Brayco 814Z	None	-	+0.1	10/5	9
460	Fomblin Z25-P28	None	-	+0.6	70/40	0
461	Fomblin Z25-P28	$C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OH$ (3-92-87)	0.5	-0.5	50/30	3
465	Brayco 814Z	None	-	0	15/30	8
466	Krytox 143AC	None	-	-0.8	90/95	0
467	Krytox 143AC	$R_f''P(O)P$ IX (3-92-92)	0.5	-0.6	65/50	4

TABLE 50 (continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

Test No.	Fluid	Additive Type[a]		Wt.%	Wt. Change mg	A%/B%	Ranking[b]
468	Brayco 814Z	None		-	-0.2	5/15	9
469	Fomblin Z25-P28	None		-	-0.1	90/95	0
470	Fomblin Z25-P28	$R_f''P(O)Ph_2$	IX (3-92-92)	0.5	-0.1	70/85	2
471	Brayco 814Z	None		-	+0.8	5/15	9
472	Krytox 143AC	None		-	-1.0	90/95	0
473	Krytox 143AC	$(R_f'')_2P(O)OPh$	XIII (3-92-125)	0.5	-0.5	80/85	1
474	Brayco 814Z	None		-	0	20/25	7
475	Fomblin Z25-P28	None		-	+0.2	85/75	0
476	Fomblin Z25-P28	$(R_f'')_2P(O)OPh$	XIII (3-92-125)	0.5	+1.0	80/75	0
477	Brayco 814Z	None		-	-0.1	3/10	9
478	Krytox 143AC	None		-	-0.3	75/70	0
479	Krytox 143AC	$(R_f')_2P(O)OPh$	VII-AI[c] (3-92-59)	0.5	+0.4	1/1	9+

TABLE 50 (continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

Test No.	Fluid	Additive Type[a]		Wt.%	Wt. Change mg	A%/B%	Ranking[b]
480	Brayco 814Z	None		-	0	5/10	9
481	Fomblin Z25-P28	None		-	+0.6	60/75	0
482	Fomblin Z25-P28	$(R_f')_2P(O)OPh$	VII-AI[c] (3-92-59)	0.6	+0.2	0/0	10
483	Brayco 814Z	None		-	+0.1	15/25	8
484	Krytox 143AC	None		-	-0.7	85/80	0
485	Krytox 143AC	$R_f''P(O)(OPh)_2$	XI (3-92-115)	0.5	+0.2	85/75	0
486	Brayco 814Z	None		-	+0.5	20/30	7
487	Fomblin Z25-P28	None		-	+0.2	85/90	0
488	Fomblin Z25-P28	$R_f''P(O)(OPh)_2$	XI (3-92-115)	0.6	+1.0	80/75	1
489	Brayco 814Z	None		-	-0.1	5/35	8
490	Fomblin Z25-P28	None		-	-0.5	80/85	0
491	Fomblin Z25-P151	None		-	-0.3	75/75	1

TABLE 50 (continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

Test No.	Fluid	Additive Type[a]		Wt.%	Wt. Change mg	A%/B%	Ranking[b]
492	Brayco 814Z			-	+0.7	5/10	9
493	Fomblin Z25-P151	None		-	0	60/45	0
494	Fomblin Z25-P151	$(R_f')_2P(O)OPh$	VII-AI[c] (3-92-59)	0.5	+1.6	0/0	10
495	Brayco 814Z	None		-	+0.9	1/1	10
496	Krytox 143AC	None		-	+0.6	35/45	0
497	Krytox 143AC	$(R_f'''')_2P(O)OPh$	XVI (1-94-31)	0.5	+0.8	35/35	1
498	Brayco 814Z	None		-	+0.2	10/25	6
499	Fomblin Z25-P151	None		-	+0.3	50/45	0
500	Fomblin Z25-P151	$(R_f'''')_2P(O)OPh$	XVI (1-94-31)	0.5	+0.7	35/40	2
501	Brayco 814Z	None		-	+0.7	5/10	9
502	Fomblin Z25-P151	None		-	0	75/75	0
503	Fomblin Z25-P151	$(R_f'''')_2P(O)Ph$	XVII (1-94-34)	0.5	+0.5	35/50	4

TABLE 50 (continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

Test No.	Fluid	Additive Type[a]		Wt.%	Wt. Change mg	A%/B%	Ranking[b]
504	Brayco 814Z	None		-	+0.2	2/5	9
505	Krytox 143AC	None		-	-0.4	40/40	0
506	Krytox 143AC	$(R_f'''')_2P(O)Ph$	XVII (1-94-34)	0.5	-0.6	40/30	1
507	Brayco 814Z	None		-	+0.2	1/0	9+
508	Fomblin Z25-P151	None		-	+0 4	50/45	0
509	Fomblin Z25-P151	$(R_f')_2P(O)Ph$	VIII (1-94-55)	0.5	+0.1	60/35	0
510	Brayco 814Z	None		-	+0.7	1/3	10
511	Krytox 143AC	None		-	-0.1	70/75	0
512	Krytox 143AC	$(R_f')_2P(O)Ph$	VIII (1-94-55)	0.5	-0.5	85/80	-1
513	Brayco 814Z	None		-	0	0/1	9+
514	Fomblin Z25-P151	None		-	-0.2	85/80	0
515	Fomblin Z25-P151	$(R_f'')_2P(O)Ph$	X (3-92-103)	0.5	-0.4	85/85	0

TABLE 50 (continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

Test No.	Fluid	Additive Type[a]		Wt.%	Wt. Change mg	A%/B%	Ranking[b]
516	Brayco 814Z	None		-	+0.1	10/30	7
517	Krytox 143AC	None		-	-0.4	80/70	0
518	Krytox 143AC	$(R_f'')_2P(O)Ph$	X (3-92-103)	0.5	-0.5	80/75	0
519	Brayco 814Z	None		-	-0.2	5/15	8
520	Demnum S-100	None		-	-0.8	55/60	0
521	Demnum S-100	$(R_f')_2P(O)OPh$	VII (1-94-52)	0.5	-0.6	50/45	2
522	Brayco 814Z	None		-	+0.2	30/35	5
523	Demnum S-100	None		-	+0.2	70/50	0
524	Demnum S-100	$(R_f'')_2P(O)Ph$	X (3-92-103)	0.5	+0.2	70/55	0
525	Brayco 814Z	None		-	+0.5	30/35	5
526	Fomblin Z25-P151	None		-	0	65/60	0
527	Fomblin Z25-P151	$(R_f')_2P(O)OPh$	VII (1-94-52)	0.5	+0.1	75/60	-1

TABLE 50 (continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

Test No.	Fluid	Additive Type[a]		Wt.%	Wt. Change mg	A%/B%	Ranking[b]
528	Brayco 814Z	None		-	-0.1	35/40	3
529	Krytox 143AC	None		-	-0.5	50/60	0
530	Krytox 143AC	$(R_f')_2P(O)OPh$	VII (1-94-52)	0.5	-0.4	65/40	0
531	Brayco 814Z	None		-	+0.7	10/15	7
532	Demnum S-100	None		-	+0.5	50/35	0
533	Demnum S-100	$(R_f')_2P(O)OPh$	VII-AI[c] (3-92-55)	0.5	+0.3	0/0	10
534	Brayco 814Z	None		-	-0.1	5/5	9
535	Krytox 143AC	None		-	-0.5	50/40	0
536	Krytox 143AC	$(R_f')_2P(O)OPh$	VII (1-94-70)	0.5	-0.6	25/30	4
537	Brayco 814Z	None		-	+0.4	15/30	6
538	Krytox 143AC	None		-	+0.1	60/40	0
539	Krytox 143AC	$(R_f')_2P(O)OPh$ (distilled; VII 66%)	VII-AS[d] (1-94-72)	0.5	+0.3	0/0	10

TABLE 50 (continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

Test No.	Fluid	Additive Type[a]	Wt.%	Wt. Change mg	A%/B%	Ranking[b]
540	Brayco 814Z	None	-	+0.5	15/35	3
541	Krytox 143AC	None	-	-0.6	30/40	0
542	Krytox 143AC	$(R_f'''')_2P(O)OPh$ XVI-AS1[d] (1-94-75) (distilled; XVI 61%)	0.5	+0.4	0/0	10
543	Brayco 814Z	None	-	-0.2	25/10	7
544	Krytox 143AC	None	-	-0.5	65/50	0
545	Krytox 143AC	$(R_f'''')_2P(O)OPh$ XVI-AH[e] (1-94-35) (XVI 64%)	0.5	0.0	0/0	10
546	Brayco 814Z	None	-	+0.2	15/10	7
547	Krytox 143AC	None	-	-0.4	45/35	0
548	Krytox 143AC	$(R_f')_2P(O)OPh$ VII-AH1[e] (1-94-77) (H_2O washed; VII 59%)	0.5	0.0	0/0	10
549	Brayco 814z	None	-	+0.1	5/5	7
550	Fomblin Z25-P151	None	-	+0.2	15/15	0
551	Fomblin Z25-P151	$(R_f'''')_2P(O)OPh$ XVI-AS1[d] (1-94-75) (distilled; XVI 61%)	0.5	0.0	0/0	10

TABLE 50 (Continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

Test No.	Fluid	Additive Type[a]	Wt.%	Wt. Change mg	A%/B%	Ranking[b]
552	Brayco 814Z	None	-	0.0	20/10	5
553	Demnum S-100	None	-	-0.5	55/10	0
554	Demnum S-100	$(R_f'''')_2P(O)OPh$ XVI-AS1[d] (1-94-75) (distilled; XVI 61%)	0.5	0.0	0/0	10
558	Brayco 814Z	None	-	+0.4	3/5	9
559	Fomblin Z25-P151	None	-	0.0	40/50	0
560	Fomblin Z25-P151	$(R_f')_2P(O)OPh$ VII-AS[d] (1-94-72) (distilled; VII 66%)	0.5	+0.6	1/0	10
567[g]	Brayco 814Z	None	-	0	15/30	6(24h)
568[g]	Krytox 143AC	None	-	-0.6	50/55	0(24h)
569[g]	Krytox 143AC	$(R_f'''')_2P(O)OPh$ XVI-AS1[d] (1-94-75) (distilled; XVI 61%)	0.5	+0.4	0/0	10(24h)
570	Brayco 814Z	None	-	+0.3	5/20	7
571	Demnum S-100	None	-	+0.3	50/30	0
572	Demnum S-100	$(R_f')_2P(O)OPh$ VII-AS[d] (1-94-79) (sublimation residue; VII 64%)	0.5	+0.5	0/0	10

TABLE 50 (Continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

Test No.	Fluid	Additive Type[a]	Wt.%	Wt. Change mg	A%/B%	Ranking[b]
573	Brayco 814Z	None	-	+0.5	5/30	4
574	Krytox 143AC	None	-	0	30/30	0
575	Krytox 143AC	$(R_f''''')_2P(O)Ph$ XVII-AS[d,f] (1-94-96-1) (distilled; XVII 98%)	0.5	-0.1	5/20	6
576	Brayco 814Z	None	-	+0.2	10/20	7
577	Fomblin Z25-P151	None	-	-0.2	50/40	0
578	Fomblin Z25-P151	$(R_f''''')_2P(O)Ph$ XVII-AS[d,f] (1-94-96-1) (distilled; XVII 98%)	0.5	-1.7	70/80	-7
579	Brayco 814Z	None	-	+0.4	5/10	8
580	Krytox 143AC	None	-	-0.4	35/30	0
581	Krytox 143AC	$(R_f''''')_2P(O)OPh$ XVI-AS2[d] (1-94-103) (distilled; XVI 81%)	0.5	+0.7	0/0	10
585[g]	Brayco 814Z	None	-	+0.3	30/40	6(24h)
586[g]	Demnum S-100	None	-	-1.0	85/80	0(24h)
587[g]	Demnum S-100	$(R_f''''')_2P(O)OPh$ XVI-AS2[d] (1-94-103) (distilled; XVI 81%)	0.5	+0.1	0/1	9^+(24h)

TABLE 50 (Continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

Test No.	Fluid	Additive Type[a]	Additive Wt.%	Wt. Change mg	A%/B%	Ranking[b]
588	Brayco 814Z	None	-	+0.2	10/15	8
589	Demnum S-100	None	-	-0.4	65/80	0
590	Demnum S-100	$(R_f'''')_2P(O)OPh$ XVI-AS3[d,h]	0.5	+0.6	0/0	10
594	Brayco 814Z	None	-	+0.8	5/10	8
595	Demnum S-100	None	-	-0.1	40/30	0
596	Demnum S-100	$(R_f'''')_2P(O)Ph$ XVII-AS[d,i] (1-94-95) (undistilled; XVII 72%)	0.5	+0.7	15/20	5
606	Brayco 814Z	None	-	+0.3	5/10	9
607	Demnum S-100	None	-	-0.7	65/50	0
608	Demnum S-100	$(R_f'''')_2P(O)Ph$ XVII-AS[d,f] (1-94-96-1) (distilled; XVII 98%)	0.5	-1.4	85/75	-4
612	Brayco 814Z	None	-	+0.3	5/5	9
613	Demnum S-100	None	-	-0.9	80/90	0
614	Demnum S-100	$(R_f'''')_2P(O)Ph$ XVII-AS[d,i] (1-94-95) (undistilled; XVII 72%)	1.5	0	20/15	7

TABLE 50 (Continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

Test No.	Fluid	Additive Type[a]	Wt.%	Wt. Change mg	A%/B%	Ranking[b]
621	Brayco 814Z	None	-	-0.1	20/35	7
622	Demnum S-100	None	-	-1.0	85/80	0
623	Demnum S-100	$(R_f'''')_2P(O)OPh$ XVI-AS2[d] (1-94-129) ($NaHCO_3$ washed; XVI 94%)	0.5	+0.4	0/0	10
624	Brayco 814Z	None	-	+0.3	1/5	9
625	Demnum S-100	None	-	-0.4	30/55	0
626	Demnum S-100	$(R_f'''')_2P(O)Ph$ XVII-AS[d] (1-94-95) (undistilled; XVII 72%)	1.5	0.0	25/30	4
642	Brayco 814Z	None	-	0.0	15/10	8
643	Demnum S-100	None	-	-0.6	60/50	0
644	Demnum S-100	$(R_f')_2P(O)OPh$ VII-AH2[e] (1-95-20) ($NaHCO_3$ washed; VII 95%)	0.5	0.0	0/0	10
645	Brayco 814Z	None	-	+0.5	40/20	4
646	Demnum S-100	None	-	-0.7	70/30	0
647	Demnum S-100	$(R_f')_2P(O)OPh$ VII-AH2[e] (1-95-22) (H_2O washed; VII 32%)	0.5	0.0	0/0	10

TABLE 50 (Continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

Test No.	Fluid	Additive Type[a]	Wt.%	Wt. Change mg	A%/B%	Ranking[b]
648	Brayco 814Z	None	-	-0.2	2/0	9
649	Demnum S-100	None	-	-0.8	30/20	0
650	Demnum S-100	$(R_f')_2P(O)OPh$ VII-AH3[e] (1-95-23) (H_2O washed; diluted 1:2; VII 77%)	0.5	0.0	0/0	10
651	Brayco 814Z	None	-	-0.3	5/2	9
652	Demnum S-100	None	-	-1.0	60/40	0
653	Demnum S-100	$(R_f')_2P(O)Ph$ VIII-AH[e] (3-92-69) (hydrolysis residue; VIII 82%)	0.5	+0.1	3/2	9
654	Brayco 814Z	None	-	-0.2	5/5	9
655	Demnum S-100	None	-	-1.3	60/40	0
656	Demnum S-100	$(R_f')_2P(O)OPh$ VII-AH4[e] (1-95-25) (H_2O washed; diluted 1:4; VII 86%)	0.5	+0.1	0/0	10
657	Brayco 814Z	None	-	+0.2	3/1	9+
658	Demnum S-100	None	-	-0.5	75/70	0
659	Demnum S-100	$(R_f')_2P(O)OPh$ VII-AH5[e] (1-95-26-2) (H_2O washed; diluted 1:4; VII 91%)	0.5	0.0	0/0	10

TABLE 50 (Continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

Test No.	Fluid	Additive Type[a]	Wt.%	Wt. Change mg	A%/B%	Ranking[b]
660[g]	Brayco 814Z	None	-	+0.1	5/2	9(24h)
661[g]	Demnum S-100	None	-	-0.5	50/30	0(24h)
662[g]	Demnum S-100	$(R_f')_2P(O)OPh$ VII-AH5[e] (1-95-26-2) (H_2O washed; diluted 1:4; VII 91%)	0.5	0.0	0/0	10(24h)
663	Brayco 814Z	None	-	-0.2	5/1	9
664	Demnum S-100	None	-	-0.4	40/20	0
665	Demnum S-100	$(R_f'''')_2P(O)OPh$ XVI-AS5[d] (1-95-44) (sublimation residue; XVI 85%)	0.5	+0.1	0/0	10
666	Brayco 814Z	None	-	-0.1	10/5	9
667	Demnum S-100	None	-	-0.9	80/70	0
668	Demnum S-100	$(R_f')_2P(O)Ph$ VIII-AS[d] (1-95-30) (sublimation residue; VIII 62%)	0.5	+0.1	1/1	9+
672[g]	Brayco 814Z	None	-	-0.1	5/3	9(24h)
673[g]	Demnum S-100	None	-	-0.5	50/40	0(24h)
674[g]	Demnum S-100	$(R_f'''')_2P(O)OPh$ XVI-AS5[d] (1-95-44) (sublimation residue; XVI 85%)	0.5	0.0	0/0	10(24h)

TABLE 50 (Continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

Test No.	Fluid	Additive Type[a]	Wt.%	Wt. Change mg	A%/B%	Ranking[b]
675	Brayco 814Z	None	-	-0.1	30/0	8
676	Demnum S-100	None	-	-0.4	80/40	0
677	Demnum S-100	$(R_f')_2P(O)Ph$ VIII-AS[d] (1-95-30) (sublimation residue; VIII 62%)	1.0	+0.1	1/1	9+
678[g]	Brayco 814Z	None	-	+0.2+	90/90	5[j](24h)
679[g]	Demnum S-100	None	-	-0.9	70/60	0(24h)
680[g]	Demnum S-100	$(R_f')_2P(O)Ph$ VIII-AS[d] (1-95-30) (sublimation residue; VIII 62%)	1.0	0.0	1/1	9+(24h)
681[g]	Brayco 814Z	None	-	+0.1	70/50	5[j](24h)
682[g]	Demnum S-100	None	-	-0.4	80/70	0(24h)
683[g,k]	Demnum S-100	$(R_f'''')_2P(O)OPh$ XVI-AS5[d] (1-95-44) (sublimation residue; XVI 85%)	0.5	0.0	0/0	10(24h)
684[g]	Brayco 814Z	None	-	0.0	90/90	5[j](24h)
685[g]	Krytox 143AC	None	-	-0.4	60/50	0(24h)
686[g,k]	Krytox 143AC	$(R_f'''')_2P(O)OPh$ XVI-AS5[d] (1-95-44) (sublimation residue; XVI 85%)	0.5	+0.1	0/0	10(24h)

TABLE 50 (Continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

Test No.	Fluid	Additive Type[a]	Additive Wt.%	Wt. Change mg	A%/B%	Ranking[b]
690	Brayco 814Z	None	-	-0.1	5/2	9
691	Demnum S-100	None	-	-0.3	60/50	0
692	Demnum S-100	$(R_f'''')_2P(O)OPh$ XVI-AS6b[d] (1-95-93) (sublimation residue; XVI 86%)	0.5	0.0	1/1	10
693	Brayco 814Z	None	-	0.0	1/1	9+
694	Demnum S-100	None	-	-0.4	50/50	0
695	Demnum S-100	$(R_f'''')_2P(O)OPh$ XVI-AS6a[d] (1-95-84) (sublimation residue; XVI 87%)	0.5	0.0	1/0	10
699[g]	Brayco 814Z	None	-	+0.1	90/90	5[j] (24h)
700[g]	Demnum S-100	None	-	-0.4	60/50	0 (24h)
701[g,k]	Demnum S-100	$(R_f')_2P(O)OPh$ VII-AH5[e] (1-95-26-2) (H_2O washed; diluted 1:4; VII 91%)	0.5	+0.1	0/0	10 (24h)
706	Krytox 143AC	$(R_f'''')_2P(O)OPh$ XVI-AS6a[d] (1-95-84) (sublimation residue; XVI 87%)	0.1	+0.1	1/0	9+
707	Krytox 143AC	None	-	-0.2	50/30	0
708	Demnum S-100	$(R_f'''')_2P(O)OPh$ XVI-AS6a[d] (1-95-84) (sublimation residue; XVI 87%)	0.1	0.0	1/1	9+

TABLE 50 (Continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

Test No.	Fluid	Additive Type[a]	Additive Wt.%	Wt. Change mg	A%/B%	Ranking[b]
720[g]	Brayco 814Z	none	-	-0.1	50/50	1(24h)
721[g]	Demnum S-100	none	-	-0.4	60/50	0(24h)
722[g]	Demnum S-100	$(R_f'''')_2P(O)OPh$ XVI-AS6a[d] (1-95-84) (sublimation residue; XVI 86%)	0.5	+0.1	0/0	10(24h)
723	Krytox 143AC	$(R_f'''')_2P(O)OPh$ XVI-AS7[d] (1-95-111) (sublimation residue; XVI 92%)	0.5	+0.1	0/0	10
724	Krytox 143AC	none	-	-0.4	50/50	0
725	Krytox 143AC	$(R_f'''')_2P(O)OPh$ XVI-AS7[d] (1-95-115) (sublimation residue; XVI 93%)	0.5	0.0	0/0	10

a) $R_f' = C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O$, $R_f'' = C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O$, $R_f'''' = C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O$.

b) Rankings are made on a scale of 0 to 10 with 0 representing a completely corroded coupon corresponding to a blank, 10 representing a total absence of corrosion and 9+ corresponding to corrosion lower than 5% of the blank. Negative values are given when the corrosion using the formulated fluid was more extensive than that of the blank.

c) This sample contains the active ingredient as an impurity and was purified by distillation only.

TABLE 50 (Concluded)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

d) In this sample the proportion of the active ingredient was predetermined in the synthesis process.
e) This sample contains the active ingredient as the result of hydrolysis by water at 100°C.
f) This sample was distilled, and contained 98% of XVII.
g) The test was conducted for a 24 h period.
h) This is a mixture containing 50% of XVI-AS2 and 50% of XVI.
i) This sample was not distilled, and contained 72% of XVII.
j) This coupon had a light brown discoloration over 90% of the metal surface. This was not the usual corrosion; the ranking of 5 given was arbitrary.
k) The fluid used in this test was formulated six months prior to testing.

period of 6 months at room temperature. No changes in appearances were noted, no cloudiness or precipitation took place. As above, thermal/oxidative stability determinations were performed on the fresh formulations and after the 6 months exposure. Additive VII-AH5 solution: fresh, 0.48 mg/g (Test 61); after 6 months, 0.38 mg/g (Test 73). Additive XVI-AS5 solution: fresh, 0.42 mg/g (Test 65); after 6 months, 0.36 mg/g (Test 72). All the tests are summarized in Table 49.

To determine the shelf life stability of the most promising corrosion inhibitors, 0.5% solutions of Additives VII-AH5 and XVI-AS5 in Demnum S-100 and a 0.5% solution of XVI-AS5 in Krytox 143AC were stored at room temperature over a six months period. No change in appearance was noted, no cloudiness or precipitation took place. After the six months storage the three solutions were subjected to 24 h CREP evaluations; in each instance a rating of 10 (total absence of corrosion) was registered. The tests are listed in Table 50; Tests 681-683, 699-701, and 684-686, respectively.

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